INTERNATIONAL ATOMIC WEIGHTS

1946

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	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26 97	Molybdenum	Mo	42	95 95
Antimony	Sb	51	121 76	Neodymium	Nd	60	144 27
Argon	A	18	39 944	Neon	Ne	10	20 183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137 36	Nitrogen	N	7	14 008
Beryllium	Be	4	9 02	Osmium	Os	76	190 2
Bismuth	Bi	83	209 00	Oxygen	O	8	16 0000
Boron	B	5	10 82	Palladium	Pd	46	106 7
Bromine	Br	35	79 916	Phosphorus	P	15	30 98
Cadmium	Cd	48	112 41	Platinum	Pt	78	195 23
Calcium	Ca	20	40 08	Potassium	K	19	39.096
Carbon	C	6	12 010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140 13	Protactinium	Pa	91	231
Cesium	Cs	55	132 91	Radium	Ra	88	226.05
Chlorine	Cl	17	35 457	Radon	Rn	86	222
Chromium	Cr	24	52 01	Rhenium	Re	75	186 31
Cobalt	Co	27	58 94	Rhodium	Rh	45	102 91
Columbium	Cb	41	92 91	Rubidium	Rb	37	85 48
Copper	Cu	29	63 57	Ruthenium	Ru	44	101 7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150 43
Erbium	Er	68	167 2	Scandium	Sc	21	45.10
Europium	Eu	63	152 0	Selenium	Se	34	78 96
Fluorine	F	9	19 00	Silicon	Si	14	28 06
Gadolinium	Gd	64	156 9	Silver	Ag	47	107.880
Gallium	Ga	31	69 72	Sodium	Na	11	22.997
Germanium	Ge	32	72 60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178 6	Tantalum	Ta	73	180 88
Helium	He	2	4 003	Tellurium	Te	52	127.61
Holmium	Ho	67	164 94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114 76	Thorium	Th	90	232.12
Iodine	I	53	126 92	Thulium	Tm	69	169.4
Iridium	Ir	77	193 1	Tin	Sn	50	118.70
Iron	Fe	26	55 85	Titanium	Ti	22	47 90
Krypton	Kr	36	83 7	Tungsten	W	74	183.92
Lanthanum	La	57	138 92	Uranium	U	92	238.07
Lead	Pb	82	207 21	Vanadium	V	23	50.95
Lithium	Li	3	6 940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174 99	Ytterbium	Yb	70	173 04
Magnesium	Mg	12	24 32	Yttrium	Y	39	88.92
Manganese	Mn	25	54 93	Zinc	Zn	30	65.38
Mercury	Hg	80	200 61	Zirconium	Zr	40	91.22

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STANDARD METHODS
OF
CHEMICAL ANALYSIS

A Manual of Analytical Methods and General Reference for the Analytical Chemist and for the Advanced Student

BY

WILFRED W. SCOTT, Sc.D.

Late Professor of Chemistry, University of Southern California. Author of "Qualitative Chemical Analysis," "Technical Methods of Metallurgical Analysis," "Inorganic Quantitative Chemical Analysis."

FIFTH EDITION

EDITED BY

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IN TWO VOLUMES, ILLUSTRATED

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PART I

SAMPLING, PRELIMINARY TREATMENT AND APPLIED ANALYSIS

STANDARD METHODS OF SAMPLING [1]

GENERAL OUTLINE FOR SAMPLING SOLIDS

INTRODUCTION

An accurate and uniform sampling procedure, applicable to all solid materials from the viewpoint of both producer and consumer, would necessitate the standardization of an infinite number of details, and probably result in a very cumbersome and impractical manipulation. It, therefore, appears advisable to first consider the various steps of the process of sampling, attempting their standardization and then applying this standardization to each particular product or group of related products.

The process of sampling is divided into three major operations:

1. The collection of the " gross " sample.
2. The reduction of the " gross " sample to a proper and convenient size for transportation to the laboratory.
3. The preparation of the sample for analysis.

These essential points and the accuracy with which they are performed determines the value of the subsequent analytical results. Experimental data and general mathematical deductions make it possible to standardize these operations with a fair degree of accuracy.

SAMPLING UNIT [2]

The sampling unit may be defined as that portion of the material which is chosen in such a manner that there is a high probability that it will contain the different sized particles of the material in the proportion in which they occur in the entire bulk of the material. Providing there are no great uncontrollable irregularities in the material, the sampling unit, if taken under carefully prescribed conditions for each different class, should be properly representative of the material. However in order to obviate the necessity of specifying in great detail, and to guard against unforeseen sectional variations in the material, it is more expedient to select a number of sampling units, these depending upon the size of the shipment to be sampled, and combine these sampling units into one large sample called the " Gross Sample."

The character of the material, size of the various particles, uniformity of composition and the prominence of any one or more constituents are factors governing the determination of the amount to be taken as the sampling unit. Without considering a mathematical discussion of the modulus of precision of a condition which would be impossible of duplication and in view of the

[1] Chapter by J. B. Barnitt.

[2] See: Chemical Analysis of Aluminum, Aluminum Research Labs., 1935, pp. 1–3. Sampling and Evaluating Secondary Metals, T. A. Wright, Am. Inst. Min. & Met. Engineers, Tech. Pub. No. 81 (1928). Also A. S. T. M. 1935 Proceedings, on Testing in the Precious Alloy Field.

experimental data compiled on the sampling of coal, it is safe to adopt, as the general sampling unit, an amount of material equal to approximately 500 times the weight of the largest particle. If this is impractical, due to the presence of very large particles, and the material cannot be reduced by passing it through a crusher, it will be necessary to reduce, by hand, the large particles at the various sampling points so that the correct proportion of large particles can be included in the sampling unit. In some cases, however, a different bulk of sampling unit will be found necessary.

COLLECTION OF THE GROSS SAMPLE

The amount of material to be included in the gross sample depends more upon the size of the individual particles than upon the size of the shipment since it is simply a multiple of the sampling unit. When the shipment is large and frequent sectional variations do not prevail, and it is being transferred by containers with a capacity approximately equal to the sampling unit, it is advisable to take the entire contents of a definite percentage of the containers as increments of the gross sample.

When the accumulated gross sample is too large to handle conveniently as a unit, it is permissible to reduce the gross sample in small sections by the standard procedure and subsequently combine the reduced portions in the correct ratio.

1. From Carload Lots

(*a*) **When the Material is to be Unloaded from Flat-bottomed Cars.**—Divide the top surface of the car into eight equal areas and, from each of these sections, take approximately the equivalent of one sampling unit in the following manner: From a stable bank of the material, beginning from the bottom, take with a shovel, at regular and equal intervals from the bottom to the top of the bank, ten equal portions of the material as specified. Combine these sampling units for the gross sample.

The stable bank may be obtained:

1. By digging down to the bottom of the car at the center of each section.
2. As the center of each section of the car is reached during the ordinary process of unloading by shoveling or otherwise.

(*b*) **When the Material is Being Transferred from or to the Car by Means of Wheelbarrows, Tram-cars, Wagons, etc.**—Take the specified increment according to the material in question from a specified number of conveying containers. Combine these increments for the gross sample. When at any point a particle is encountered which is larger than the specified increment it should be broken down and a portion of it included in the sample.

(*c*) **When the Material is Dumped from a Hopper Car into a Hopper, Bin or Pile.**—Under these conditions, the sample is taken from the resulting cone-shaped pile by beginning at the bottom outer edge of the pile and taking the specified increment, according to the character of the material, every two feet on a straight line to the apex of the cone. This operation is repeated on each quadrant of the pile. The entire procedure is repeated after each car has been dumped and all increments combined for the gross sample.

2. From Wheelbarrows, Barrels, Bags, Tram Cars, Carts, Trays, etc.

(*a*) From a specified number of containers, take the specified increment and combine them for the gross sample.

(*b*) Take the entire contents of every *n*th container and combine them for the gross sample.[3]

(*c*) If the material is fairly uniform [4] and composed of small particles, sample the container by taking ten equal specified increments uniformly distributed on two right angle diagonals across the surface of the container. Sample the specified number of containers in this way and combine the several portions for the gross sample.

3. From Crane Buckets, Cars, Carts and Similar Containers, Chutes, etc.

(*a*) If one container amounts to less than one sampling unit, take every 10th load and combine these for the gross sample.

(*b*) If one container amounts to approximately 1–3 sampling units, take every 20th load and combine these for the gross sample.

(*c*) If one container amounts to more than three sampling units, take every 50th load and combine these for the gross sample. Note: When very large shipments are being sampled by the above procedures very large gross samples will result which would be difficult or inconvenient to reduce to the laboratory sample. In this case the gross sample may be reduced periodically as follows. At regular intervals, representing a definite number of tons, the gross sample is quartered, one quarter reserved and three quarters returned to the main bulk. The total combined quarters thus reserved are mixed by shoveling into a cone-shaped pile and then further reduced by the Standard Procedure to the laboratory sample.

(*d*) When the material is composed of particles one inch or less in size, take a specified increment from every *n*th container.

(*e*) When the material is being dumped into a crusher from which it flows or is flowing, from a drying kiln or other process kiln, the material may be sampled by taking specified increments from the outflowing stream at stated regular intervals.[5]

4. From Shipholds, Scows, Hoppers, Hopper-cars, Bins, Storage Piles, etc.

In this case the material may be sampled in any of several ways.

(*a*) According to the previous section 3, while loading or unloading.

(*b*) According to the section 1, for carloads while unloading or loading.

(*c*) While using material from a storage pile, daily or periodic samples may be taken as follows: On ten vertical lines from the bottom to the top of the face of the pile distributed at uniform distances across the face, take ten equal

[3] In cases where experience indicates the procedure to be justifiable, it may be permissible to take a portion of the contents of every *n*th container.

[4] Relatively few materials are sufficiently uniform to be sampled in this manner.

[5] A more thorough method of sampling is used for materials containing precious metals.

specified increments at equal distances from bottom to top. Combine these increments for the gross sample over any desired period.

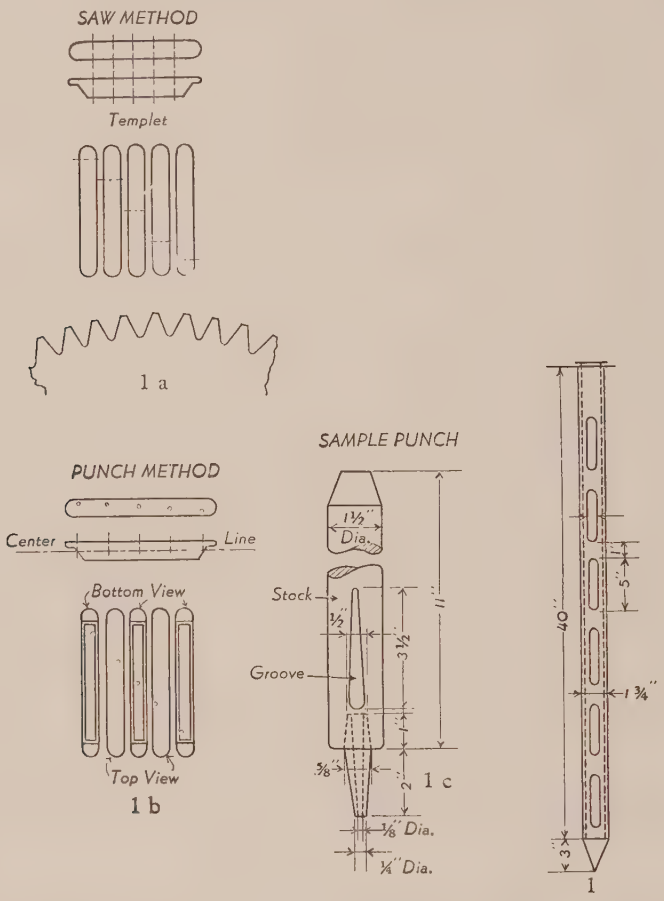

Fig. 151. Apparatus for Sampling Solids.

Sect. 1. Thief for sampling solids ¼″ diameter or smaller. Openings to correspond. Both tubes hollow and to be made from $\frac{1}{16}$″ sheet brass (hard). Inside tube to fit snugly into outside tube. Point to be steel or iron.

Sect. 1*a*. Saw Method of Sampling Pigs. The bars are sampled in sets of five, according to Template as shown. Saw is sharpened on Emery Wheel to size and shape here shown.

Sect. 1*b*. Punch Method of Sampling Pigs.[6] The bars selected as samples are placed in a line, with every other bar, bottom side up. The sampling is done according to template in sets of five bars each, as indicated above. The punch must be driven almost through the bar. If a large sample is desired, the bars are turned over and sampled on the other diagonal.

Sect. 1*c*. Sample Punch.

[6] Lead is best sampled when molten ("gum-drop" method) rather than in pig form.

5. For Powdered Material

When the material is a fine powder or is composed chiefly of material under 2 mm. and contains a small amount of unsegregated particles up to 10 mm. in the largest dimension, the sampling unit is taken by means of a specially designed thief (Fig. 151) or by means of a suitable shovel, dipper, etc.

(*a*) From large shipments, as shipholds, scows, barges, cars, etc. On a line through the center of the holder lengthwise, take portions with the thief every five feet. Repeat this operation on each of two lines parallel with and half way between the first line and each side of the holder. Combine all the portions for the gross sample. If the shipment is composed of more than one holder, combine the portions from each holder into a composite gross sample.

(*b*) From tram cars, carts, buggies, etc.

Take a specified portion from each holder with the thief or shovel and combine all portions for the gross sample.

(*c*) From barrels, bags, wheelbarrows, etc.

Take a portion from every *n*th container and combine the portions for the gross sample.

(*d*) From small piles (not more than six feet in height).

With the thief, take one portion vertically at the peak of the pile and one vertically at each of ten points uniformly distributed along a line around the pile half-way between the peak and the edge of the pile. Combine these portions for the gross sample.

(*e*) From a well-mixed bulk of material (from mixers, packing machines, etc.).

After allowing a specified quantity, according to the condition of the material and type of apparatus, to flow past the sampling point, take the specified quantity for a sample. Periodic samples may be taken in the same manner, as often as desired.

6. From Wet Material

Wet materials arrange themselves in several classes:

When the material is thoroughly wet but not dripping, take the sample by any of the foregoing suitable procedures, keeping the collected portions in moisture-tight containers.

(*a*) When water is dripping from the material, take the sample as prescribed for the particular material by one of the foregoing procedures and allow the total gross sample to drain, the drainage and remainder of the sample being weighed and recorded. If further elimination of water is necessary either by air drying, artificial drying or pressing, before the gross sample is reduced to the laboratory sample, the total water eliminated must be calculated and taken into account in the final evaluation of the material to the original wet condition. In case this water carries some of the material in solution, it will be necessary to ascertain the amount of this by analysis and include the results in the final evaluation.

(*b*) When fine solid material is non-uniformly suspended in a liquid several vertical sections of the material may be taken by means of a specially designed thief and combined for the gross sample. (See general outline for sampling liquids.)

7. From Hygroscopic or Deliquescent Materials

(*a*) When such material is contained in airtight containers which may be readily opened and closed, take a sample by means of a thief (Sect. 1), when the material does not contain resistant particles, larger than ½ inch in cross section or, otherwise, by means of a small scoop or shovel. These increments should be placed and retained in an air-tight receiver until ready for the analysis.[7]

(*b*) When such material can be sampled while being transferred to the final container for shipment, small and equal increments at uniform and regular intervals, are taken directly from the stream by means of a suitable dipper and combined for the gross sample.

8. From Kilns, Roasters, Dryers, Furnaces, etc.

This class of material constitutes a special case, and, consequently the size of sampling unit and manner by which it may be taken will be specified according to the size of particles and character and condition of the material.

9. Sampling Non-ferrous Metals and Alloys[8]

(*a*) **In the Form of Pigs, Billets, Ingots, Sheets, Slabs, etc.**—One pig, etc., should be taken to represent each ton of metal in the lot and each of these should be sampled by one of the following methods after thoroughly cleaning the surface to be sampled.

1. By sawing completely through the specimen as illustrated by Sect. 1*a*, Fig. 151. The sawdust from all the specimens is then thoroughly mixed and quartered down on a clean surface and the required amount of sample drawn.

2. By punching or drilling completely through if the equipment permits, or halfway through from two opposite sides as illustrated by Sect. 1*c*, 1*b*, Fig. 151. In this case the holes shall be spaced along a diagonal line from one corner of the specimen to the other. Sampling in this manner may be so arranged that one or more holes are made in each of several specimens of a group in such positions that they represent consecutive positions on the diagonal of a single specimen. (See illustration in Sect. 1*c*.) These punchings or drillings are carefully melted in a clean graphite crucible, and either granulated by carefully pouring into distilled water and thoroughly drying, or by casting into thin slabs which may be sawed completely through in several places and the sawdust treated as described above. Drillings may be chipped and mixed if convenient.

(*b*) **In the Form of Sheets.**—In sampling brass discs, and sheets, when they can be crated so that the edges are flush, recourse can be made to a portable milling machine operated by a ¼ H.P. electric motor run transversely across the edges, so adjusted that only a very thin milling is taken from each disc or sheet. These are coned and quartered for the sample. By this method the serviceability of the disc or sheet is not destroyed, and the completeness

[7] Readily oxidizable material must be stored in similar fashion (iron pyrites, etc.).

[8] See E. Keller, Bur. Mines Bulletin, **122** (1916), 105 pp. For steels, ores, etc., see Methods of the Chemists of the U. S. Steel Corporation for Sampling and Analysis of Iron Ores, etc. Publ. by Carnegie Steel Co., Pittsburgh, Pa. See A. S. T. M., E 30–36, pp. 2–6, Methods of Chemical Analysis of Metals (1936).

of the sampling depends only on the accuracy of adjusting the edges in the crate.

PROCEDURE FOR REDUCING THE GROSS SAMPLE

By combining the several sampling units, the gross sample is obtained which should now be so large that large single chance particles of material could be entirely foreign matter or entirely pure substance and affect only slightly if at all the final sample. Increasing the size of the gross sample increases its accuracy, but cost and convenience of collection and reduction of sample, limit the degree to which this can be carried to advantage. The reduction of the gross sample to the laboratory sample is an operation which must be performed with accuracy and precision. Automatic machinery and labor and time saving devices may be used for this operation adhering closely to the following general scheme with the exception that some materials of uniform comparison need not be finally reduced as small as 6 mm.—4 mesh—while it may be necessary to finally reduce other material to .14 mm.—100 mesh—or finer.

In sampling large shipments, the gross sample may become excessively large and unwieldy. This may be obviated by periodically reducing the gross sample by the Standard Long Pile and Alternate Shovel Procedure, and subsequently compositing these reduced portions for the final gross sample.

REDUCTION OF THE GROSS SAMPLE

(Approx. 1000 lbs.) crushed to about 22.6 mm.—1 mesh; thoroughly mixed and halved by the Long Pile and Alternate Shovel procedure.

Discard	One-half crushed to about 16 mm.—1.5 mesh; mixed and halved by
½	the Long Pile and Alternate Shovel procedure.
½	One-half crushed to about 11.3 mm.—2 mesh; mixed and halved by the Long Pile and Alternate Shovel procedure.
½	One-half crushed to about 4 mm.—5 mesh; mixed by rolling on canvas; halved by Cone and Quartering procedure.
½	One-half ground to about 2 mm.—10 mesh; mixed by rolling on canvas; halved by riffling (or sampling machine) or by the quartering procedure.
½	One-half mixed and riffled down to about 8 lbs.

The entire eight pounds is then further reduced and the required sample taken according to the character of the particular material.

A portion for the determination of moisture may be taken at some point during the reduction according to the character of the sample and manner in which the moisture test is made. When a moisture sample is wanted it is necessary that the sampling units be collected and stored under conditions whereby moisture would not be lost or absorbed. The mixing, crushing and halving operations, preceding the taking of the sample for moisture should be accomplished as rapidly as possible.

In case the gross sample contains an excessive amount of water which would be lost in the subsequent operations necessary to reduce it to the laboratory

sample, it should be kept in a tight container during the collection of the various increments, after which it is weighed and allowed to air-dry, or it may be dried artificially, and reweighed. It is then in a condition to be reduced to the laboratory sample according to the above scheme, taking into account, of course, the moisture thus driven off from the original gross sample in the final calculation for the evaluation of the material.

REDUCTION OF GROSS SAMPLE (LONG PILE AND ALTERNATE SHOVEL)

This procedure is based upon the method recommended and used by the U. S. Bureau of Mines.

FIG. 152. Method of Sampling Ore.

1. Thoroughly mix the entire gross sample, after crushing in a suitable manner until all pieces are approximately one inch or less in any dimension, by shoveling it into a cone-shaped pile, depositing each shovelful on the apex of the pile (Fig. 152, *A* and *B*).

2. Shovel all of the material into a pile about the width of the shovel and approximately 10 feet long according to the total amount of material, spreading each shovelful uniformly over the whole length of the pile, beginning alternately from opposite ends (Fig. 152, *C*).

3. Divide the long pile into two equal portions by beginning on one side of the pile, at either end, and take successive shovelfuls, advancing each time by the width of the shovel around the pile, combining the first and every alternate shovelful into a neat cone-shaped pile as in No. 1 and discarding the second and every alternate shovelful (Fig. 152, *D* and *E*).

4. Repeat the above operation on the reserved portion until a portion of about 500 lbs. is obtained.

5. Crush the material until no piece is greater than approximately three-fourths inch in any dimension, and then repeat the above operation (No. 3).

6. Crush the material until no piece is larger than approximately one-half inch in any dimension and then repeat the above operation (No. 3).

7. A portion of about 125 lbs. is now obtained which is further reduced by the "Cone and Quartering Procedure."

REDUCTION OF GROSS SAMPLE (CONE AND QUARTERING)

1. Mix the material amounting to about 125 lbs. by crushing to pass a 4 mm.—5 mesh—sieve and shoveling into a neat cone (Fig. 152, *F* and *G*).

2. Flatten the cone by pressing the apex vertically down with the shovel or board so that, when quartered, each quarter will contain the material originally contained therein.

3. Divide the flattened pile into equal quarters by passing a straight edge board vertically twice through center of the pile at right angles, each time drawing half of the pile a few inches to one side (Fig. 152, *H* and *I*).

4. Discard two opposite quarters and brush away all fine particles from the exposed surface (Fig. 152, *J*).

5. Crush the remaining quarters to pass a 2 mm.—10 mesh—sieve. Mix thoroughly by shoveling into a neat cone.

6. Repeat operations No. 3 and 4 or riffle to about 20 pounds.

7. Grind the retained sample to pass a .85 mm.—20 mesh—sieve. Mix the material thoroughly on a clean canvas by raising alternate opposite corners of the canvas, thus rolling the material from side to side one hundred times (Fig. 152, *K* and *L*).

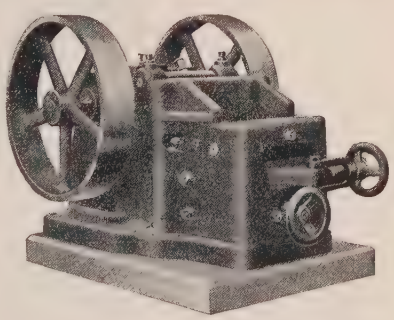

FIG. 153.[9] Jaw and Toggle Crusher for Coarse and Medium Fine Grinding.

8. Treat the sample further as required by the particular material being sampled.

[9] Courtesy of Sturtevant Mill Co.

It is, of course, impossible to reduce hygroscopic or deliquescent gross samples to the laboratory sample according to the above scheme unless they can be dried or otherwise transformed into a stable condition. When it is necessary to reduce such material it should be done rapidly and by hand, under the most favorable atmospheric conditions in regard to humidity, etc. When a large sample is taken for analysis the extent of the reduction of the sample will depend upon the size of the sample taken for analysis.

APPARATUS FOR REDUCTION AND PREPARATION OF THE SAMPLE

Any sampling system which does not properly control the ratio of the size of largest particle to the size of sample can not be depended upon to produce a representative sample. The proper ratio for almost all material will be obtained by following the procedure outlined under the heading " Procedure for Reducing the Gross Sample." This reduction process is greatly facilitated by the use of suitable crushers, grinders, riffle samplers and mixing devices. The following examples of such apparatus are therefore given as an aid to the designing and equipping of the sampling room, the size and capacity of which will be determined by the number, character, and size of the gross samples to be handled.

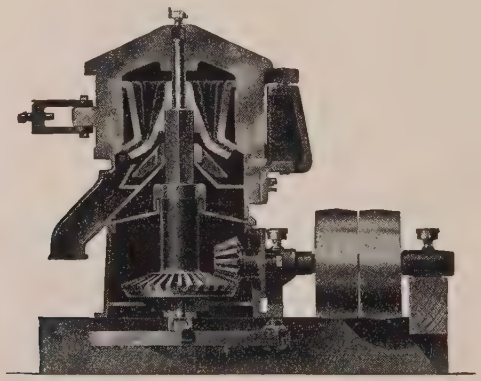

FIG. 154.[10] Crusher and Grinder in Cross Section.

Crushers.—A jaw and toggle crusher is shown in Fig. 153. This is a satisfactory crusher for coarse, medium and fine crushing and permits a considerable range of adaptability to suit varying conditions and requirements. Simple adjustments allow the capacity to be varied from about 200 pounds per hour for the production of fine material to 700 pounds per hour for coarser material when considering only one of the several sizes of this type of crusher. The parts are readily accessible for cleaning and repairing. By means of this type of crusher it is possible to reduce the material to about 4 mesh.

[10] By courtesy of Sturtevant Mill Co.

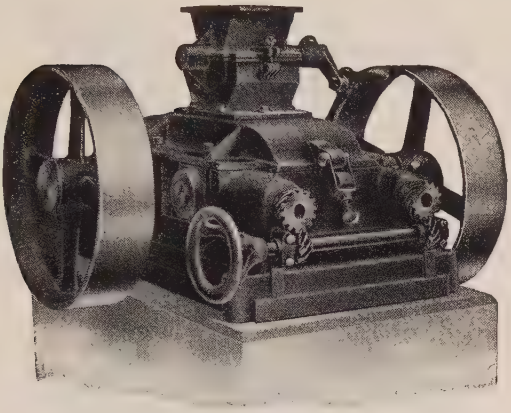

FIG. 155.[11] Roll Grinder for Brittle Material.

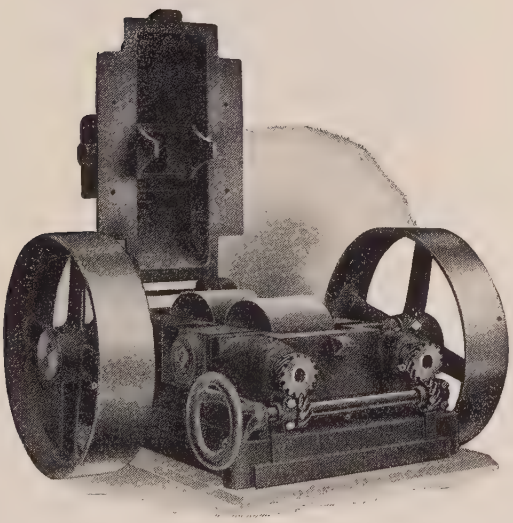

FIG. 156. Roll Grinder with Case Lifted to Show Interior.

[11] By courtesy of Sturtevant Mill Co.

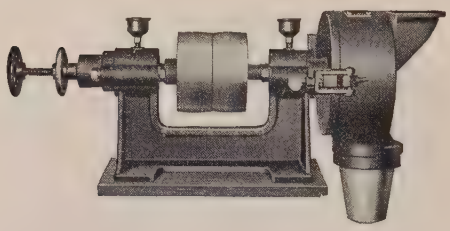

FIG. 157.[12] Disc Grinder Ready to Run.

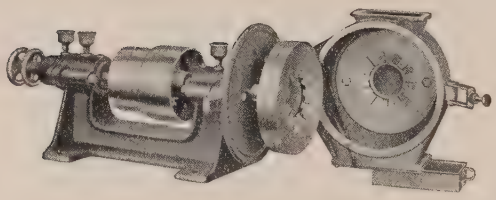

FIG. 158.[12] Disc Grinder Open for Cleaning.

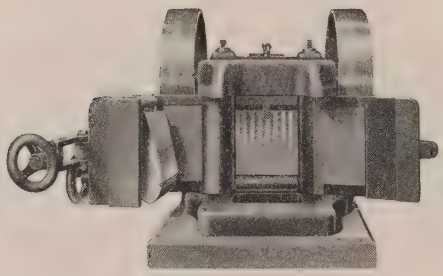

FIG. 159.[13] Crusher Open for Cleaning.

[12] By courtesy of Sturtevant Mill Co.
[13] By courtesy of Sturtevant Mill Co.

Grinders.—*Grinders* are necessary for reducing the material finer than 4 mesh and may be of the roll, disc or coffee mill type, according to the character of the material.

Roll grinders are especially adapted for brittle material. Figures 155 and 156 illustrate a type of roll grinder which may be readily cleaned and has a capacity of 100 to 1,000 lbs. per hour when producing a reduction to a fineness of 60 mesh and 2 mesh respectively. Disc grinders have a somewhat greater range of adaptability than the roll grinder and will reduce brittle or tough material to a high degree of fineness. The grinding is accomplished between a stationary and a revolving steel or iron disc, the output being small and fine or large and coarse according to the adjustment. Figures 157 and 158 illustrate a satisfactory type of disc grinder.

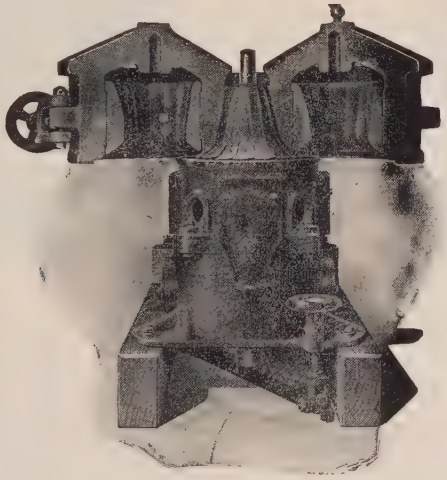

Fig. 160. Combination Crusher and Sampler.

The coffee mill type of grinder is adaptable to soft or tough materials which have a tendency to stick to the rolls of the roll grinders or to clog the discs of some types of disc grinders. Many kinds of coffee mill type grinders have been developed from which selection can be made according to the character of material under consideration. Figures 155 and 157 illustrate very good coffee mill types. When reducing material to extreme fineness the ball mill, special small laboratory grinders, the bucking board and mortar and pestle are always applicable for small samples.

Another type of crusher and grinder which has been developed particularly for sampling coal is shown by Fig. 154. This crusher will reduce the material and deliver an accurate ten per cent sample in one operation. By repeating the operation on the aliquot the sample may be further reduced.

For many materials this crusher would serve to entirely reduce the gross sample to the laboratory sample with a very small amount of labor.

MIXING AND DIVIDING SAMPLES

Large samples (500 lbs. or more) are usually mixed and divided by the "Long Pile and Alternate Shovel" procedure or (500–100 lbs.) by the "Cone and Quartering" procedure.

Small samples (less than 100 lbs.) are usually mixed by rolling on a clean canvas, whereby the particles are given a rolling motion in alternately opposite directions, the dividing being done by quartering or, more accurately and rapidly, by passing it through some form of a riffle. A convenient and serviceable type of riffle is illustrated by Fig. 161. Another and more simple type is shown by Fig. 162.

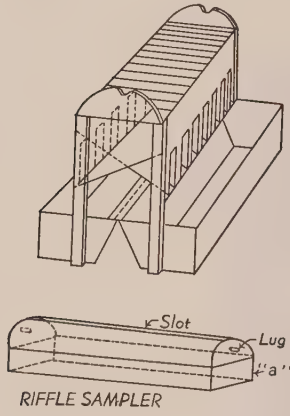

Fig. 161.

Fig. 162.

Fig. 161. Riffle Sampler. "*a*," cover to fit tightly over one of the boxes with slot in rounded tops—also fitted with two lugs which fit in ends of riffle and help to rock evenly.

Fig. 162. The cut shows the apron of the cylinder of this machine open for receiving the sample. After the sample is poured in, the apron's position is shifted, *a* being moved to *a'*. The cylinder is then revolved counterclockwise. The closed sides of the riffles plow through and thoroughly mix the sample, and no sample can be discharged through the riffle while the cylinder is revolving in this direction if the level of the sample is below the axis of the cylinder. After the sample has been mixed the cylinder is rotated one turn clockwise; the sample in the cylinder is then cut by the planes of the riffle and half of it is discharged into the receiving tray. The sample remaining is again mixed by revolving the cylinder counterclockwise. By alternately changing the direction, the sample is alternately mixed and halved until twice the size of sample required remains in the cylinder. The tray is then emptied of the discarded material, and the sample remaining, mixed and halved, and the sample caught in the tray is bottled and becomes the official sample, while the sample remaining in the cylinder is bottled and held as the reserve sample. The interior of the machine is easy of access and should be brushed clean after each sampling operation.

THE USE OF STANDARD SIEVES

This section is based upon the specifications issued by the U. S. Bureau of Standards (1912) and adopted by the Amer. Inst. of Mining Engineers (1917).

The essential quantity in the definition of a sieve of a particular size is, primarily, the size of the openings through which the particles to be sifted are to pass.

A series of sieves of different sizes should have the openings vary uniformly, according to the size of the particles desired to separate. Inasmuch as most of the grinding of substances to fine particles is chiefly with the object of increasing the surface upon which some chemical action is to take place, the opening of such a series of sieves should vary in such a way that the square or fourth powers of the width of the openings shall form a geometrical series.

Designation of Sieve, Metric System	Customary Usage	Opening		Number of Mesh per Linear		Diameter of Wire	
		Mm.	Inch	Centimeter	Inch	Mm.	Inch
128 mm.		128.0	5.04			9.5	0.375
90.5 mm.		90.5	3.56			9.5	0.375
64 mm.		64.0	2.52			6.4	0.25
45.3 mm.		45.3	1.78			5.26	0.207
32.0 mm.		32.0	1.26			4.85	0.192
22.6 mm.	1 mesh	22.6	0.891			4.11	0.162
16.0 mm.		16.0	0.630			3.05	0.120
11.3 mm.	2 mesh	11.3	0.445			2.67	0.105
8.0 mm.		8.0	0.315	1.0	2.54	2.00	0.079
5.66 mm.		5.66	0.223	1.4	3.56	1.48	0.058
4.00 mm.	5 mesh	4.00	0.157	2.0	5.10	1.00	0.039
2.83 mm.		2.83	0.111	2.75	7.00	0.81	0.032
2.00 mm.	10 mesh	2.00	0.079	3.9	9.9	0.56	0.022
1.41 mm.		1.41	0.0555	5.0	12.7	0.59	0.0232
1.00 mm.		1.00	0.0394	7.0	17.8	0.43	0.0169
.85 mm.	20 mesh	0.85	0.0335	8.0	20.3	0.40	0.0157
.71 mm.		0.71	0.0280	9.0	22.9	0.40	0.0157
.59 mm.		0.59	0.0232	10.0	25.4	0.41	0.0161
.5 mm.	30 mesh	0.50	0.0197	12.0	30.5	0.33	0.0130
.42 mm.		0.42	0.0165	14.0	35.6	0.29	0.0114
.36 mm.	40 mesh	0.36	0.0142	16.0	40.6	0.26	0.0102
.29 mm.	50 mesh	0.29	0.0114	20.0	50.8	0.21	0.0083
.25 mm.	60 mesh	0.25	0.0098	23.0	58.4	0.185	0.0073
.21 mm.	70 mesh	0.21	0.0083	27.0	68.6	0.16	0.0063
.17 mm.	80 mesh	0.17	0.0067	31.0	78.7	0.15	0.0059
.14 mm.	100 mesh	0.14	0.0055	39.0	99.1	0.116	0.0046
.125 mm.	120 mesh	0.125	0.0049	47.0	119.4	0.089	0.0035
.105 mm.	150 mesh	0.105	0.0041	59.0	149.9	0.064	0.0025
.088 mm.	170 mesh	0.088	0.0035	67.0	170.2	0.061	0.0024
.074 mm.	200 mesh	0.074	0.0029	79.0	200.7	0.053	0.0021
.062 mm.	250 mesh	0.062	0.0024	98.0	248.9	0.040	0.0016
.052 mm.	280 mesh	0.052	0.0021	110.0	279.4	0.039	0.0015
.044 mm.	325 mesh	0.044	0.0017	127.0	323.0	0.035	0.0014

While the sampling process does not require extremely accurate sieves it is advisable to use those which conform approximately to a standard specification. Consequently whenever reference is made to a sieve it will be understood to comply with the following specifications, which have been adopted by a conference of representatives of various scientific and technical societies, government bureaus, and private firms, held at the U. S. Bureau of Standards.

This sieve scale is essentially metric. The sieve having an opening of 1 mm. is the basic one and the sieves above and below this in the series are related to it by using in general the square root of 2 (1.4142), or the fourth root of 2 (1.1892), as the ratio of the width of one opening to the next smaller opening. The first ratio is used for openings between 1 mm. and 128 mm. while the fourth root of 2 is used as the ratio for openings below 1 mm. to give more sieves in that part of the scale.

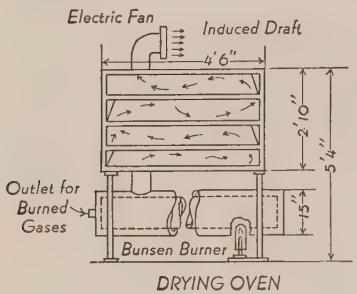

Fig. 163. Dryer for Coarse Samples. The outlet for air at the top may be connected with a chimney or any other device which will furnish a suitable draft. The sample is spread on tared pans, weighed, and dried at 10° to 15° C. above room temperature, and weighed again. The drying should be continued until the loss in weight is not more than 0.1 per cent per hour.

CONTAINERS FOR SHIPMENT TO LABORATORY

Samples in which the moisture content is important should always be collected and shipped in moisture-tight containers. A galvanized iron or tin can with a screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit-jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit.

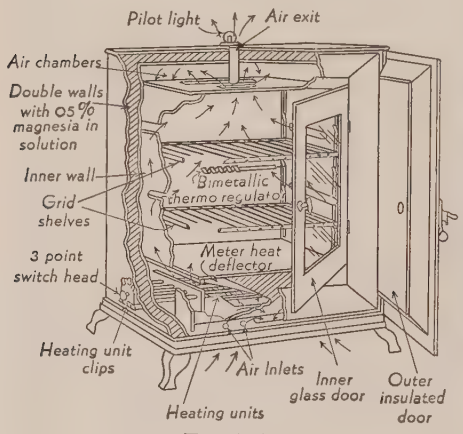

Fig. 164.

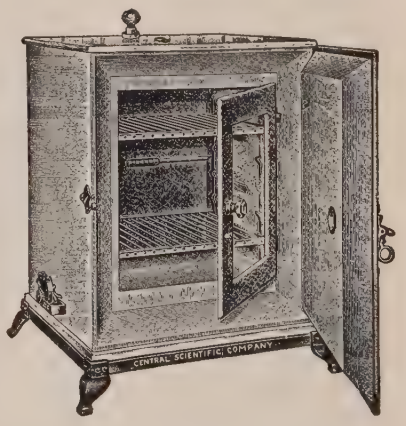

Fig. 165.

Figs. 164 and 165. Drying oven, triple walled, with a layer of air entirely surrounding the inner chamber, the temperature of this layer being practically the same as that of the air in the chamber. This approaches an adiabatic construction which has been approved by the Bureau of Standards as the best type of design for calorimeters and other constant temperature devices. By this construction together with a heavy outer insulation, heat exchanges between the inner chamber and the room outside are practically entirely prevented, and as a result of uniformity of temperature is secured in the heated space. The drying chamber should be entirely shielded from direct radiation from the heating units, and into every part of which heat should be carried by convection currents.

Samples in which the moisture content is of no importance need no special protection from loss of moisture.

DRYING OVENS FOR MOISTURE DETERMINATION

Samples may be dried by means of a forced draft of air at a slightly elevated temperature, or by heating at 100–110° C. in a well-ventilated oven until a constant weight is obtained. The former procedure is particularly adapted to material which has a tendency to undergo undesirable chemical or physical changes upon prolonged heating at elevated temperatures or for rapidly removing extraneous moisture preparatory to grinding. The latter procedure is usually employed for quantitative determinations on small finely ground samples. In either case a good system of ventilation and a definite uniform temperature are the chief considerations.

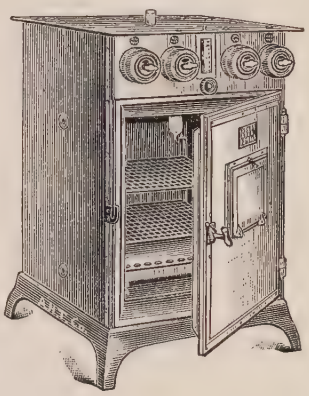

FIG. 166.[14]

High Temperature Ovens, for operation from room temperature to 260° C.

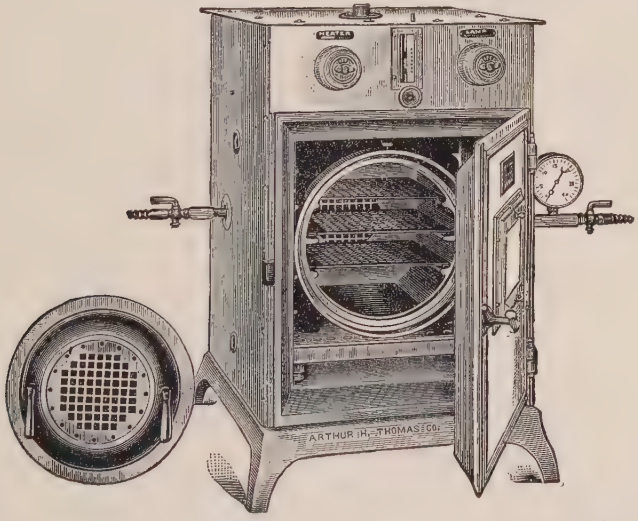

FIG. 167.[15] Vacuum oven. Supplied with a vacuum chamber which may be easily removed, permitting the oven proper to be used as a regular drying oven when the vacuum feature is not desired. Moisture test of flour can be made in five hours at 75° C., while in an ordinary oven at 100° C. from ten to twelve hours are required. The same conditions apply for organic tests in general, i.e., for fertilizers where the tests must be made at the lowest possible temperature to avoid driving off nitrogen compounds; for powder where there is great danger of igniting the sample; for milk where there is great danger of charring; for operations involving essential oils, etc.

When tests are to be conducted in an atmosphere of hydrogen, nitrogen, carbon dioxide or other gas, it is only necessary to pass a current of the desired gas through the vacuum chamber.

[14] By courtesy of Arthur Thomas Co.

[15] By courtesy of Central Scientific Co.

Figure 163 illustrates an oven for drying large samples by means of a current of heated air. Figures 164 and 165 show a type of oven with a good ventilating system. Figure 166 shows another type of oven, while 167 illustrates a vacuum drying oven which may be necessary for special work.

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GENERAL OUTLINE FOR SAMPLING LIQUIDS

In general, a uniform and representative sample of liquid material is a feasible possibility because of the usual absence of segregated constituents, the ease with which the separate components may be intimately mixed, and the degree of comminution to which a liquid may be subjected without producing a separation of the individual components.

When the liquid is thin, non-viscous, and does not contain immiscible constituents, a homogeneous condition usually exists, and a sample from any part of the bulk is sufficiently representative of the whole. When viscous or immiscible materials are present, a heterogeneous condition usually exists and extreme care must be exercised to obtain a thoroughly representative sample. The proper selection of a representative sample of a liquid therefore, involves a consideration of the physical laws of liquids, their chemical activity, the

miscibility of all components, and the interference of any insoluble materials carried by the liquid.

The sampling of liquids is divided into the three following classes; sampling liquids in quiescent state, sampling liquids in motion, sampling special liquors, e.g., immiscible liquids, volatile liquids, liquids carrying sediment, etc.

SAMPLING LIQUIDS IN QUIESCENT STATE

All liquids not in motion may be sampled by obtaining portions at specified points from the top to the bottom of the liquid by means of a suitable sampling apparatus.

1. From Storage Tanks, Tank Cars, Boats, Evaporating Kettles, Vats, Crystallizers, Mixers, Settlers, etc.

(*a*) If the liquid has been thoroughly agitated or is known to be reasonably uniform in composition, transfer several portions to a container by means of a suitable dipper, the several dippings being taken promiscuously throughout the mass of liquor.

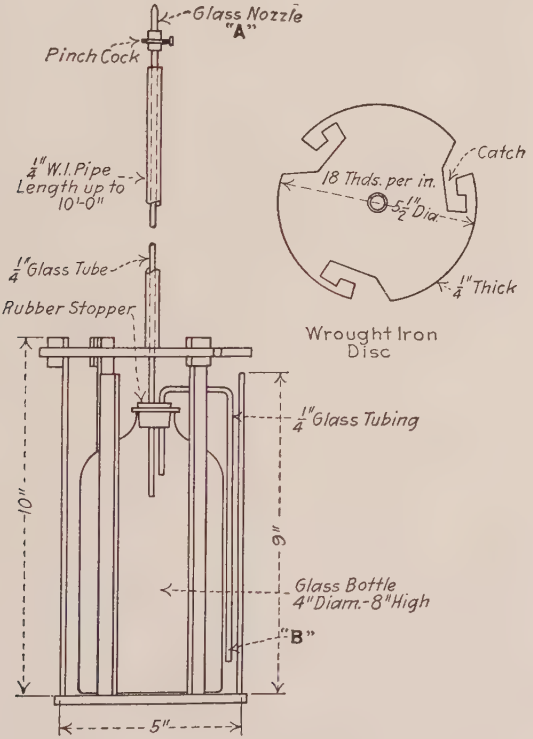

Fig. 168. Sampling Liquids Apparatus

(*b*) If the character and condition of the liquid is such as to permit the formation of zones of different composition, obtain samples by means of a suitable apparatus as shown by Fig. 168, whereby proper proportions of the liquid are taken at every point from the top to the bottom. Combine these samples for the gross sample and, after thoroughly mixing, bottle the required samples (Fig. 168). By slowly lowering the sampling bottle into the liquid with the outlet (*A*) open, a portion of the liquid from every point passes through (*B*) into the bottle, whereas if outlet (*A*) is kept closed until the desired depth is reached, the entire sample may be taken at any desired point.

Lead, wood, or any other material which is resistant to the liquid may be substituted for the iron parts of this device, according to the character of the liquid being sampled. Under some conditions it will be necessary to substitute a ground glass stopper for the rubber one. Openings of different sizes can be attached at (*A*) to govern the rate at which the sample will flow into the bottle.

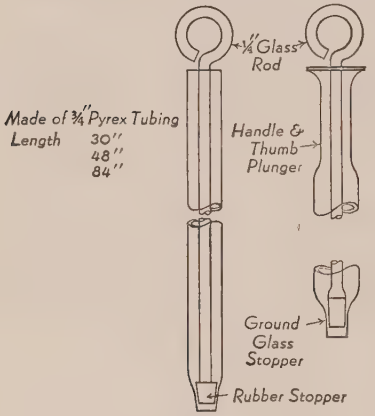

Fig. 169. Sampling Liquids Apparatus.

(*c*) Take a sample from the upper, middle, and lower levels of the liquid by means of a sampling device similar to that shown by Fig. 168, by keeping the outlet tube *A* closed until the container has been lowered to the desired depth.

2. From Drums, Carboys, Barrels, etc.

(*a*) By means of a thief (Fig. 169) take proportional fractions from each container. Combine and mix these increments for the composite gross sample. Bottle the amount required for the sample. If the contents of the container are such as to preclude thorough mixing or if the material has a tendency to form strata of varying compositions, the open thief should be lowered into the liquid at such a rate as to keep the levels of liquid inside and outside of the thief very nearly equal, in order to include portions at all points from the top to the bottom of the liquid.

SAMPLING LIQUIDS IN MOTION

3. From a Pipe or Conduit Carrying a Continuous Full Flow under a Constant or Varying Head

(*a*) A continuous or intermittent sample may be taken by inserting a small pipe into the line on the discharge side of the pump or propelling force of the flow. This sampling tube should extend one-half of the distance to the center of the flow, with the inner open end turned at an angle of 90° and facing the flow of the liquid. The sampling tube may be supplied with a stopcock in order to regulate the flow into a receiver. The amount drawn during the period of taking a continuous sample constitutes the gross sample. In this instance the stopcock should be adjusted at the beginning of the sampling period, to give the desired flow and no readjustment made during the

sampling period. Intermittent samples may be taken by opening the stopcock for a definite period of time at definite intervals. The combined intermittent samples then constitute the gross sample.

4. From a Pipe or Conduit Carrying a Varying Fraction of Flow

(*a*) By means of a sampling weir similar to the apparatus shown by Fig. 171, a definite fraction of varying flow can be collected over a required period

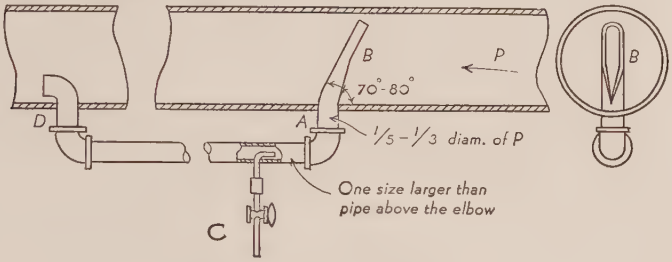

Fig. 170. Apparatus for Sampling Liquids in Motion.

of time. This gross sample may be mixed and a portion taken for the final sample or by connecting two or more of the above devices in series; a small representative sample may be collected automatically, e.g., if one million gallons of liquid per day are passing through a pipe or conduit line at an irregular rate, it could be sampled by conducting the stream to a series of four sampling weirs, each of which separates 5% or 1/20 of the flow. A final six gallon sample would then represent the entire million gallons. The size of each weir should be such as to give a suitable overflow and the apron over which the flow passes for division should be fixed in a horizontal position.

(*b*) By means of the arrangement illustrated by Fig. 170, an approximate sample ratio can be continuously diverted from a non-uniform flow. This device consists of a pipe *A*, inserted into the flowing stream at an angle of 70–80° provided with an opening *B* facing the flow and extending to the top of pipe *P*. This opening *B* is constructed as shown in the cut (Fig. 170), the width above the center of pipe *P* being equal to the diameter of pipe *A*, then tapering from the center to the bottom of the pipe *P*. As the flow passes pipe *A*, an approximately constant sample ratio is diverted through pipe *A* and is sampled by a small pipe *C*, the opening of which faces the flow at a point halfway between the center and bottom of pipe *A*. Pipe *C* is fitted with a stopcock whereby the amount of the sample flow through *C* may be regulated. Pipe *A* reenters pipe *P* at some point which will give sufficient positive flow-head through *A*. While this arrangement will not necessarily produce an accurate sample ratio, an increased flow through *P* will increase the flow-head through *A* and consequently increase the amount of sample withdrawn at *C* and an approximately relative sample ratio will be maintained with one regulation of stopcock *C*.

(*C*) With large pipes and large flows, the above arrangement may be modified as shown by Fig. 172. Three pipes, 1, 2, and 3, bent at 90° angles with openings facing the flow at different levels are inserted in pipe *P* and connected

to a common pipe A. The flow through A is then sampled by a pipe C as described above. An approximately relative sample ratio is thus maintained with one regulation of stopcock C.

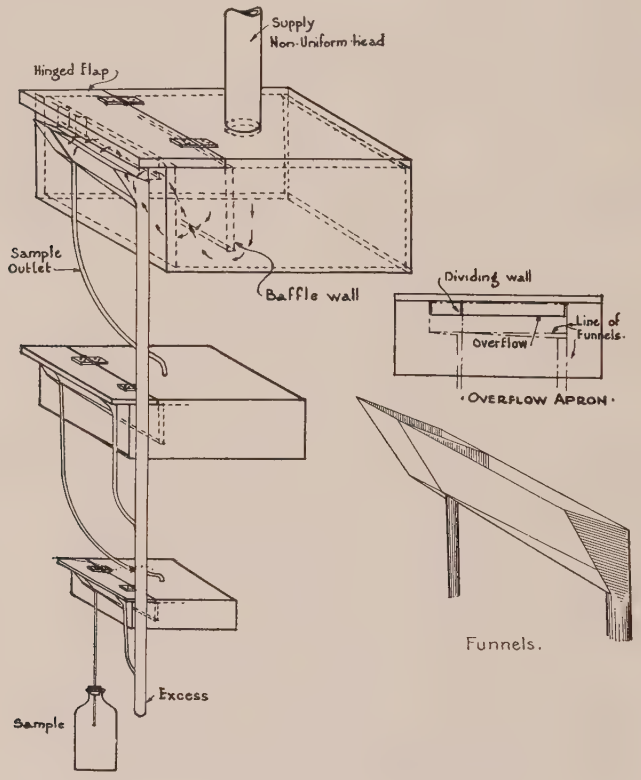

FIG. 171. Apparatus for Sampling Liquids.

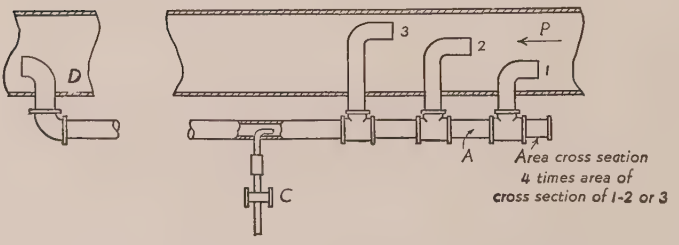

FIG. 172. Apparatus for Sampling Liquids in Motion.

SAMPLING SPECIAL LIQUIDS

5. Liquids Containing Insoluble Matter in Suspension

(*a*) When the sediment remains in reasonably uniform suspension during the period required for taking the sample, the liquid is thoroughly mixed and the sample obtained by one of the foregoing procedures.

(*b*) When the sediment settles rapidly or is impossible of uniform distribution it is necessary to take special precautions to secure the components of the sample in the proper proportion. This can be accomplished with a fair degree of accuracy by mixing the liquid thoroughly and then rapidly taking a complete column of the liquid by means of the special thief or device shown by Fig. 168 or 169. By repeating this operation a number of times, a fairly representative sample will be obtained. Another procedure of possible application under certain conditions would be to take several portions at as many uniformly distributed points from the top to the bottom by means of the thief (Fig. 168 or 169). These portions are then combined and mixed for the gross sample.

(*c*) To accurately sample a liquid containing insoluble matter, it is necessary to filter the entire liquid, weigh the insoluble material and filtrate separately and then take separate samples of the sediment and liquid, recording the ratio of sediment to liquid for use in the final evaluation of the original material. This, however, is impracticable except in such instances wherein the size of sample allows of economical handling in the manner described.

6. Liquids Composed of Immiscible Layers

The most practical and accurate procedure in this case is to effect a separation of the layers and combine portions of each layer in the proper ratios. If this is impossible, the material may be transferred to a container of uniform cross section, the depth of each layer measured, and then the proper portion taken from each layer, for a composite sample, by means of a sampling thief similar to those shown in Figs. 168 and 169.

7. Liquids Containing Crystals Due to Supersaturation

Frequently conditions are such that a portion of the liquid or certain constituents thereof have crystallized in the container. Oleum and acetic acid are common examples of this class. When practical the material should be warmed sufficiently to dissolve completely or melt the crystals before sampling by one of the foregoing procedures. Otherwise, if the crystals are small and remain in suspension the mass should be sampled as a liquid containing insoluble matter in suspension.

8. Volatile Liquids

(*a*) Volatile liquids are best sampled from a continuous flow while the liquid is being discharged or by means of a siphon from containers. If the liquid is uniform in composition or can be made so by agitation in some manner, a portion may be run to the bottom of the sampling bottle until the bottle overflows through another tube from the top into another bottle or to the

waste pipe, to such an extent as to leave a liquid in the first bottle containing the maximum amount of the volatile constituent (see Fig. 173). The sample bottle should then be quickly stoppered and sealed for transportation to the laboratory.

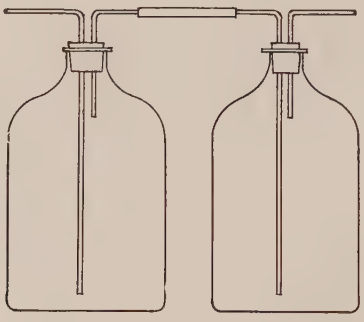

FIG. 173. Apparatus for Sampling Liquids.

REFERENCES

"Sampling Creosote Oil." Amer. Soc. Testing Materials (1918), p. 721.
"Liquid Sampling Specifications." Am. Gas Light J., **103**, 391.
"Standard Methods for the Sampling and Analysis of Commercial Fats and Oils." J. Ind. Eng. Chem., **11**, 116 (1919).

GENERAL OUTLINE FOR SAMPLING GASES

The proper sampling of gases often presents greater difficulties than the analysis. This is particularly true when it is desirable to obtain a representative sample of a gas during a considerable period of time as it passes through a pipe or flue from the source of production. Gases travel through straight pipes and conduits in an irregular succession of waves with a spiral motion, the maximum velocity being at the center of the pipe and the minimum near the walls. The motion of these waves and point of maximum velocity is altered in a varying degree by every bend and obstruction throughout the line of travel. Where gases are encountered which are subject to temperature changes either above or below normal, this factor will also considerably interfere with proper sampling. The temperature of gases will vary throughout the cross-section of the pipe, usually being hottest at points of maximum velocity and coldest next to the walls and in dead pockets. Theoretically if it were possible to discharge the total gas to be sampled into a large holder and provide time for it to thoroughly diffuse, it would then be in the most ad-

vantageous condition whereby a true and representative sample could be obtained by simply withdrawing a portion. Unfortunately this is not often the condition under which gases are to be sampled, being usually sampled from a flow possessing varying velocity, temperature, and composition. Under such conditions it is practically impossible to determine a point of approximate average velocity, temperature or composition from which a representative instantaneous sample can be drawn.

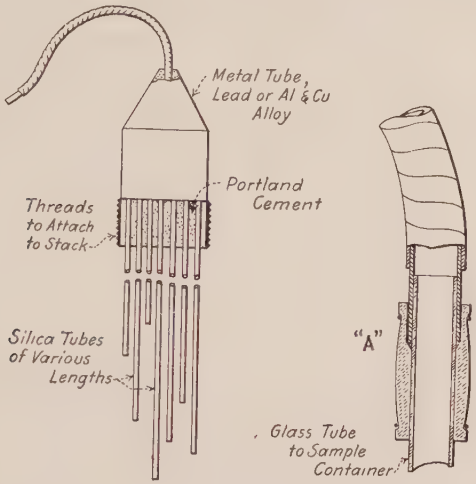
Metal Tube, Lead or Al & Cu Alloy
Portland Cement
Threads to Attach to Stack
Silica Tubes of Various Lengths
"A"
Glass Tube to Sample Container

FIG. 174. Apparatus for Sampling Gas.

Consequently it becomes necessary to collect a sample over an extended period whereby the number of series of gas waves sampled is such that there is a high probability that a true and representative sample will be obtained. Under some conditions, useful and more definite data regarding composition and gas-flow is obtained by taking frequent " grab " samples. It is, therefore, quite evident that the subject of gas sampling naturally divides itself into two phases for consideration that of continuous sampling and " grab," or instantaneous, sampling.

1. General Considerations and Apparatus

(*a*) **Sampling-tube for Drawing Samples from Gases Flowing through Pipes.**—Without discussing the merits of the various forms of sampling tubes such as the single-opening tube, and the various types of perforated tubes all of which are more or less useful under certain conditions, the multiple type originated by A. H. White—" Gas and Fuel Analysis "—is apparently best adapted for securing uniform samples (see Fig. 174). This tube should be inserted so that the longest tube reaches the center of the flowing gas.

(*b*) **Collecting a Representative Continuous Sample.**—In order that the sample should be truly representative of the total gas flowing during a definite period, it is necessary to constantly draw a definite proportion of the gas.

Great elaboration of apparatus and equipment would be necessary if the rate of drawing the sample were adjusted to vary directly with the velocity of the gas, in which case the sample would accurately represent the gas. The most practical approach to this ideal condition would be to take the continuous sample under a constant pressure, whereby the rate of sampling will vary directly with the pressure of the gas being sampled.

Figure 175 illustrates a common form of apparatus whereby a stream of gas at constant pressure is drawn from a gas line. This apparatus consists of a pressure-gage *B* to indicate any obstruction of the sampling tubes, a bubbling-bottle *C* to give a visual control of the rate of the stream, a gas-

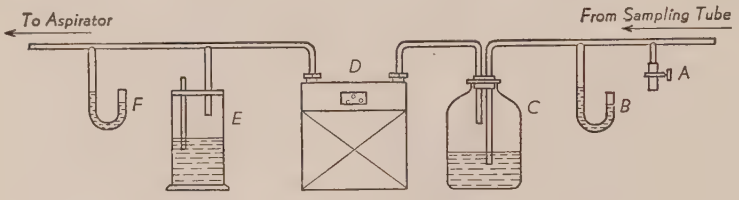

FIG. 175. Apparatus for Sampling Gas.

meter *D* which may be omitted if not needed, a pressure control, *E* and a pressure gage *F* on the line to the aspirator. When aspiration is necessary the pressure at the sampling-tube as shown by gage *B* should be only a few tenths-of-an-inch of water. This may be regulated by the depth to which the tube is immersed in the water of the regulator *E*. When the gas is under pressure, the aspirator and *E* and *F* become unnecessary.

(*c*) **The Design of Apparatus.**—The design of apparatus—and the sampling procedures—must take into account the solubility and chemical activity of the gas. Saturated magnesium chloride solution, glycerine and water mixtures, and various oils have been used with varying success in overcoming the solubility of gases in the solutions over which they are collected. Further investigations along these lines for specific gases will probably make possible the use of other liquids than mercury for gases having high solubility factors. The corrosive character of the individual gases will determine the type of containers, etc., which may be used.

2. Taking a "Grab" Sample

(*a*) For a "grab," or instantaneous, sample the ordinary two-bottle aspirator may be used (see Fig. 176) using care not to draw the sample so fast as to produce a reduced pressure at gage *B* (Fig. 175).

3. Taking a Continuous Sample

(*a*) For continuous sampling the apparatus illustrated by Fig. 177 will be found convenient.

This apparatus consists of two large galvanized metal tanks, one in the form of an aspirating-bottle in which the sample is taken, and the other, slightly larger, which acts as a reservoir. A sample of gas taken under constant pressure and at a uniform rate over any specified period of time, which

may be varied at will, is obtained by filling the tanks with water, oil or other liquids according to the character of the gas, until the level reaches the top of the aspirating-tank. A syphon acts as the outlet and a uniform rate, if the pressure of the gas in constant, is obtained by attaching it to a wooden float. The speed of outflow may be regulated by the length of the syphon and the opening or size of the outlet-nozzle.

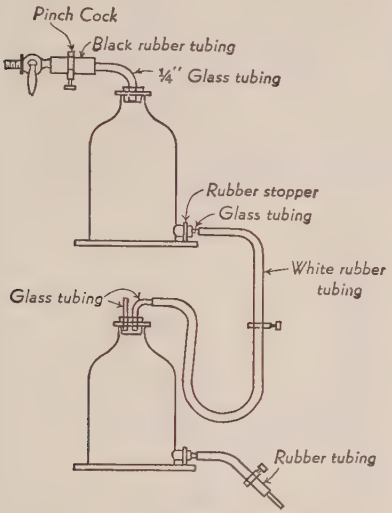

FIG. 176. Apparatus for Sampling Gas.

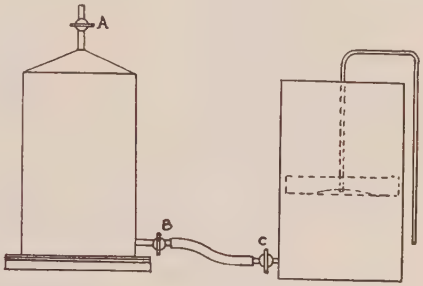

FIG. 177. Apparatus for Sampling Gas.

By arresting the downward movement of the float and syphon by means of a shoulder or suitable device, a small amount of water remains in the aspirator; this acts as a seal and automatically discontinues the intake of gas. By closing the stopcocks *A* and *B* the operation is completed.

These tanks may be constructed to crate, in compact form for transportation, a 20-liter glass aspirating-bottle, as shown in Fig. 178.

This bottle is to be used when the gas to be sampled would attack the metal aspirating-tank. If a layer of some non-absorbing oil is placed on the surface of the water the original composition of the gas is unaffected.

(*b*) When mercury must be used because of the solubility of the gas in water, an apparatus similar to that illustrated by Fig. 179, originated by Thomas Gray, J. Soc. Chem. Ind., **32**, 1092, will be found convenient.

" It consists essentially of an ordinary gas-sampling tube *N*, attached to a reservoir *J*, which is counterpoised by a vessel *R* floating in a tank *Q*, the float being connected with *J* by means of a cord which passes over the pulleys *P*.

" The float *R* may be a tinned-iron vessel or glass bottle containing the necessary quantity of water or lead shot to establish the balance. The height of the tank *Q* must be greater than the length of the sampling-tube *N*, the overflow-tube *I* should be slightly longer than *N*, and the length of the wider tube *H*, which merely serves to prevent loss of mercury by splashing, should slightly exceed that of *I*.

" The jet *V*, under pressure which may be regulated by adjustment of the overflow *W*, through which the excess of water from *U* escapes to the waste, delivers sufficient water during the specified period to raise the level in the tank to a height equal to the length of the sampling-tube.

" As the water-level rises, the reservoir J is steadily lowered, drawing the gas uniformly into the sampling tube, and the mercury, thus displaced, escapes through the overflow-tube I to the bottle G. By means of an aspirator a rapid current of gas is drawn along the tube F which is connected to the flue or gas-main by means of the sampling tube (Fig. 179), a suitable filter being interposed, if necessary, to retain any solid particles. The connection A, between the sampling tube and the tube F, is preferably made of capillary tubing 3 to 4 inches long, to prevent the diffusion of the gas backwards from N to F. If desired, a small non-return mercury valve may be inserted at this point.

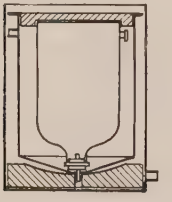

Fig. 178. Apparatus for Sampling Gas.

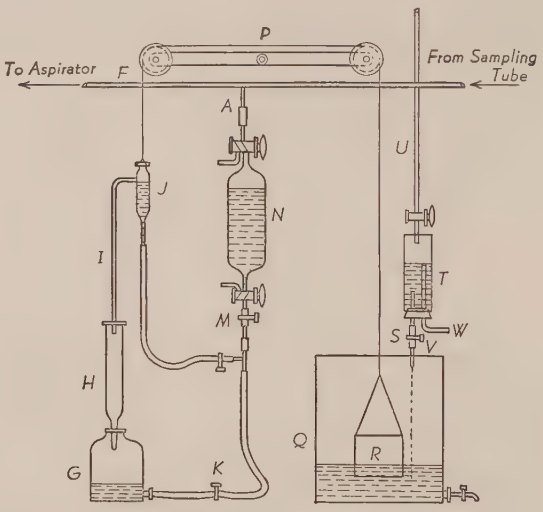

Fig. 179. Apparatus for Sampling Gas.

" To start the apparatus, the tube F is connected with the gas supply and a rapid current of gas is drawn through F by means of the aspirator.

" The rubber tube connecting the jet V with the water-supply is then closed by the clip S, and the water is allowed to run into T and to overflow freely through W the height of which has previously been adjusted to the desired level. Water is now run from the tank Q until the top of the overflow-tube I is at the level of the shoulder of the gas tube N, and J and N are now filled with mercury by means of a small funnel in J. The capillary A is finally filled with mercury by raising the reservoir J, the lower stopcock of the sampling-tube is closed, and J is then lowered to its former position and filled to the overflow-tube with mercury; the operation of sampling may now be commenced by opening the lower stopcock of the gas tube N and starting the flow of water from the jet. The aspirator and the water-supply to T remain in operation during the whole period of the test and the apparatus requires no further attention.

" The period of sampling may be varied in a number of different ways:

(1) " Jets may be constructed to deliver the requisite quantity of water in specified times; these are easily drawn from glass tubing in a blowpipe-flame, the final adjustment being effected by altering the head of water in T.

(2) " Tanks of various diameters may be employed.

(3) " The height of the sampling tube N may be varied."

REFERENCES

Sinnatt, F. S., "A Convenient Apparatus for Obtaining an Average Sample of Gas and for Regulating the Flow of a Gas into an Evacuated Vessel." Analyst, **37**, 250.
Gray, Thomas, "An Automatic Gas Sampling Apparatus." J. Soc. Chem. Ind., **32**, 1092.
White, "Gas and Fuel Analysis." International Chemical Series.

The author desires to acknowledge his indebtedness to J. S. Coye for his assistance in preparation of this chapter.

STANDARD SPECIFICATIONS FOR SIEVES FOR TESTING PURPOSES [16]

A. S. T. M. Designation: E 11–26 [17]

Sieves for precision testing have a variety of uses, including both dry screening and wet screening of material. The primary object is to separate materials according to the size of particle. Since particles are three dimensional and the openings of screens are areas having two dimensions only, the method of separation by means of screens is at best an approximation. In many instances, however, it is the best practical means at hand, and will give useful and reliable results if care is taken in securing representative samples, in the preparation of the sample for testing, in the details of procedure and in the method of reporting results. In the Appendix are indicated those points which must be considered in specifying sieving tests for any individual material.

An essential in each method, however, is a series of sieves of known characteristics. The important consideration in sieves is the size of opening and with the size of opening known it is possible to translate the results obtained in one series of sieves into terms of another series. The importance of the size of opening in the sieve series covered by these specifications is emphasized by designating the sieves in terms of opening in microns. This new scheme of designation should accordingly cause no confusion, giving as it does a direct indication of the size of opening. As such, it is not open to the objections to the various arbitrary number designations heretofore in use and it is also free from the objection to the designation by means of mesh in that it is independent of the size of wire.

[16] Under the standardization procedure of the Society, these specifications are under the jurisdiction of the A.S.T.M. Committee E-1 on Methods of Testing.

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[17] These specifications are issued under the fixed designation E 11; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1925; Adopted, 1926.

With the size of opening known, the method of recording results is simplified. It is recommended that in reporting sieve analyses in graphic form the sizes of sieve opening be arranged as ordinates with the largest size at the top and that the percentages be plotted as abscissas.

1. **Scope.**—These specifications cover sieves for use in the usual cases of precision testing for the fineness of materials (classification of materials according to size). The sieves have been designated according to the size of openings in terms of microns, the corresponding United States Standard Sieve Series designation in arbitrary numbers being given for the convenience of those familiar with the latter scheme of designation.

PHYSICAL REQUIREMENTS

2. **Cloth and Frame.**—Wire cloth for standard sieves shall be woven (not twilled, except that the cloth of 44, 53 and 62-micron sieves may be twilled until further notice) from brass, bronze, or other suitable wire and mounted on the frames without distortion. To prevent the material being sieved from catching in the joint between the cloth and the frame, the joint shall be smoothly filled with solder, or so made that the material will not catch. The sieve frames should be circular, about 20 cm. (8 in.) in diameter and about 5 cm. (2 in.) or 2.5 cm. (1 in.) between the top of the frame and the cloth.

NOTE.—The size specified above is for the regular standard testing sieve, but for special purposes other sizes may be used, as for example, the 3-in. sieve which is designed especially for use on laboratory balances as in the testing of pigments.

3. **Permissible Variations.**—The average opening between the adjacent warp and the adjacent shoot wires, taken separately, shall be that given in column 3 (or 4) of Table I, within the " Tolerance in Average Opening " given in column 7. The average diameter of the warp and of the shoot wires, taken separately, of the cloth of any given sieve shall be that given in column 5 (or 6) of Table I within the " Tolerance on Wire Diameter " given in columns 8 and 9. The maximum opening between adjacent parallel wires shall not exceed the nominal width of opening for that sieve by more than the " Tolerance in Maximum Opening " given in column 10 of Table I.

WORKMANSHIP

4. The sieves shall be free from imperfections in the sieve cloth or its mounting, as for example, punctured, loose or wavy cloth, imperfections in soldering, etc.

MARKING

5. The sieves shall bear a label upon which the manufacturer's nominal opening in metric units (preferably in microns) with the equivalent in inches, together with the size of wire should be given.

NOTE.—It is recommended that, until the new micron designation shall have been thoroughly established, in addition the corresponding United States Standard Sieve Series number be given.

TABLE I

REQUIREMENTS FOR SIEVE OPENINGS AND WIRE DIAMETERS WITH PERMISSIBLE VARIATIONS

Designation	Corresponding U. S. Standard Sieve Series Number	Sieve Opening		Wire Diameter		Tolerance in Average Opening, per cent	Tolerance on Wire Diameter, per cent		Tolerance in Maximum Opening, per cent
		mm.	in.	mm.	in.		Under	Over	
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
4760 micron	4	4.76	0.187	1.27	0.050	±3	15	30	10
4000 "	5	4.00	0.157	1.12	0.044	±3	15	30	10
3360 "	6	3.36	0.132	1.02	0.040	±3	15	30	10
2830 "	7	2.83	0.111	0.92	0.036	±3	15	30	10
2380 "	8	2.38	0.0937	0.84	0.0331	±3	15	30	10
2000 "	10	2.00	0.0787	0.76	0.0299	±3	15	30	10
1680 "	12	1.68	0.0661	0.69	0.0272	±3	15	30	10
1410 "	14	1.41	0.0555	0.61	0.0240	±3	15	30	10
1190 "	16	1.19	0.0469	0.54	0.0213	±3	15	30	10
1000 "	18	1.00	0.0394	0.48	0.0189	±3	15	30	10
840 "	20	0.84	0.0331	0.42	0.0165	±5	15	30	25
710 "	25	0.71	0.0280	0.37	0.0146	±5	15	30	25
590 "	30	0.59	0.0232	0.33	0.0130	±5	15	30	25
500 "	35	0.50	0.0197	0.29	0.0114	±5	15	30	25
420 "	40	0.42	0.0165	0.25	0.0098	±5	15	30	25
350 "	45	0.35	0.0138	0.22	0.0087	±5	15	30	25
297 "	50	0.297	0.0117	0.188	0.0074	±6	15	35	40
250 "	60	0.250	0.0098	0.162	0.0064	±6	15	35	40
210 "	70	0.210	0.0083	0.140	0.0055	±6	15	35	40
177 "	80	0.177	0.0070	0.119	0.0047	±6	15	35	40
149 "	100	0.149	0.0059	0.102	0.0040	±6	15	35	40
125 "	120	0.125	0.0049	0.086	0.0034	±6	15	35	40
105 "	140	0.105	0.0041	0.074	0.0029	±8	15	35	60
88 "	170	0.088	0.0035	0.063	0.0025	±8	15	35	60
74 "	200	0.074	0.0029	0.053	0.0021	±8	15	35	60
62 "	230	0.062	0.0024	0.046	0.0018	±8	15	35	90
53 "	270	0.053	0.0021	0.041	0.0016	±8	15	35	90
44 "	325	0.044	0.0017	0.036	0.0014	±8	15	35	90

NOTE.—Sieves having larger openings than those included in the table may be specified, but in specifying sieves of larger openings the actual size of the opening (in millimeters or in inches) shall be stated. A tolerance of ±3 per cent on average openings and of 10 per cent in maximum openings shall be permitted.

METHODS OF TESTING

6. (*a*) To determine whether the cloth conforms to the requirements of these specifications, the wire diameter shall be measured in each direction by means of a micrometer-microscope or projection apparatus or other suitable apparatus of requisite precision, care being taken in all cases to avoid diffraction effects in measuring to the edge of a wire. Micrometer calipers and steel scales should not be used for this purpose. The mesh shall be determined by

counting the number of openings for a distance of at least 6 in. in both directions of the sieve, using a scale, either glass or steel, and a microscope. The use of scales with special rulings for obtaining mesh by counting "interference bands" is recommended in cases where large numbers of any of the sieves with the smaller openings are to be measured. From the wire diameter and the mesh the average opening shall be computed.

NOTE.—No general rule can be given for the number of observations to be taken, except that they be sufficient to cause no change in the result if say 3 or 4 additional measurements are made.

(*b*) Measurements of large openings shall be made by means of the micrometer-microscope or the projection lantern or other suitable apparatus in the same way as wire diameters are measured.

NOTE.—In order to insure the securing of standard sieves it is possible to obtain from the manufacturer or dealer sieves which have been certified by the National Bureau of Standards.

APPENDIX

LIST OF POINTS TO BE CONSIDERED IN DRAWING UP SPECIFICATIONS FOR A SIEVING TEST

I. APPARATUS.

1. Enumeration of sieves to be used.
2. Auxiliary apparatus required for collection and reduction of gross sample, sample containers, and apparatus other than the sieves used in making the tests.

II. SAMPLING.

1. Unit of sampling.
2. Method of collecting representative gross sample.
3. Size of gross sample.
4. Cautions to be taken in handling sample to prevent contamination or change.
5. Reduction of gross sample.

III. PREPARATION OF THE SAMPLE FOR TESTING.

1. Drying.
2. Mixing.
3. Special treatment, if any is necessary.
4. Selection of test portion.
5. Size of test portion.

IV. PROCEDURE.

A. Dry Screening:

1. Order in which the sieves are to be used.
2. Detailed description of method of shaking.
3. Detailed description of procedure other than method of shaking.
4. End point.

B. Wet Screening:

1. Liquid to be used.
2. Description of any preliminary separation by classification or other means.
3. Order in which screens are to be used.
4. Detailed description of procedure including amount and method of adding liquid, method of stirring or other agitation.
5. End point.

V. Method of Reporting Results.

VI. Allowable Variations Between Duplicate Tests on the Same Material.

DECOMPOSITION OF THE SAMPLE [1]

Decomposition of the Material.—In the instructions for the solution of the material special procedures are often given owing to the predominance of some particular compound or compounds present. Directions are given for example for oxides, others for sulfides, and again others for silicates, etc. The chemist is frequently at loss to know what procedure to select as the mere inspection of the material frequently will furnish him no information as to its predominating trait.

Owing to the variables in ores and alloys it is not possible to have any set procedure applicable to all conditions. It is often necessary to combine two or more methods to effect solution of certain refractory ores. Acid extractions are frequently followed by fusion methods for the solution of the acid insoluble material, likewise fusions require subsequent water extraction followed by acids. In general, ores should be finely ground, before treatment by wet or fusion method. The following general rules, however, will be of value.

General Procedure.—It is advisable to test the solubility of a small amount of the material in a test tube, using water if the material is a salt or hydrochloric acid if an ore, and dilute nitric acid if an alloy or metallic product. In examining an ore the sample should be finely powdered. About 0.5 to 1.0 gram is taken and treated with 10 to 20 ml. of concentrated hydrochloric acid. A pear-shaped flask, of pyrex glass, is convenient for this decomposition. The solution is heated gently until no further action is evident. If the ore contains sulfur as sulfide, the addition of nitric acid and bromine are recommended, nitric acid in most cases follows the addition of hydrochloric acid, but in case of sulfur determination, nitric acid and bromine are added first to avoid loss of sulfur as H_2S. For alloys dilute nitric acid precedes HCl. Additional HCl and HNO_3 may be necessary to complete the possible action of these acids. Dilute sulfuric acid is now added and the solution evaporated to near dryness. This generally effects complete decomposition. If a residue remains upon adding HCl and water and heating, it is advisable to filter off the solution and fuse the residue by one of the fluxes given under " Fusions," page 1336. It is often advisable to start with a fusion of the original ore—sodium and potassium carbonate for high silicon ores, sulfates of barium, strontium and calcium; potassium acid sulfate fusions made preferably in a pyrex glass flask for oxides of metals. In case of refractory oxides decomposition is assisted by adding a small piece of filter paper to the molten mass.

[1] Original chapter by Wilfred W. Scott.

Reagent to Effect Solution — *Materials*

I. Water will dissolve the alkali salts, ammonium, lithium, potassium and sodium acetates, bromides, chlorates, chlorides, iodides, nitrates, nitrites, sulfates. Also arsenates, arsenites, borates, carbonates, oxalates, phosphates, and tartrates. The halides of silver, mercury, and lead are insoluble in water. The arsenates, arsenites, borates, carbonates, oxalates, phosphates and tartrates of the heavy metals require acid treatment to effect solution. Sulfates of Ba, Sr, Ca, Hg″, Pb are insoluble in water.

II. Acids

1. *Hydrochloric acid* decomposes carbonate and oxide ores of B, Ca, Fe, Mn, Mg, P, Sn (reducing agt.), Ti, U, Zn ($SnCl_2$ assists Fe sol.).
2. *Hydrochloric acid* together with or followed by an *oxidizing reagent*, i.e., HNO_3, $KClO_3$, etc. Alloys of Al, Sb, Bi, Cu; Cr, Co and Ni steels, ferro silicon, Ti and V steels, sulfide ores of Cu, Ce, Pb, Mo, U, Zn.
3. *Nitric acid*, dilute or concentrated. Alloys of Bi, Cd, Co, Cu, Pb, Mn, silico manganese, ferro manganese, P and Ti steels, ores of Cd, Cu, Mo, Co and Ni.
4. *Aqua Regia.*—The metals and alloys of Au, Ir, Hg, V, Pt. Ores of Cd, Hg, Rh, W.
5. *Sulfuric acid.*—Ores of Al, Be, Mn, Pb, Th, Ti, U.
6. *Sulfuric acid* with HF, silicates, Cu ores and alloys.
7. *Hydrofluoric acid*, usually in conjunction with H_2SO_4, HCl or HNO_3 useful for dissolving ores containing silicates where SiO_2 is not to be determined. An $HF-HNO_3$ (5 : 5 : 200 H_2O) is an excellent solvent for antimony-tin alloys.
8. *KBr, Br, HNO_3, HCl* combinations to dissolve pyrites of Pb, Ni, Fe, As, etc. Reactions 1–8 (excepting 7) may be made in glass; 7 in platinum.
9. Constant-boiling hydriodic acid, sp.gr. 1.70, attacks many of the slightly soluble substances: HgS with brisk evolution of H_2S; SnO_2 with evolution of SnI_4; the hot acid transposes the silver halides, the majority of the "insoluble" sulfates (Pb; Ca; Sr; Ba; Cr); dissolves CaF_2; $CrCl_3$ (anhydrous), etc.[2]
10. Perchloric acid is a powerful oxidizing and also a dehydrating agent when hot and concentrated. The solubility of the majority of the perchlorates in water makes the acid a very desirable solvent. The perchlorates in general are soluble in organic solvents such as alcohols, ketones, aldehydes, ethers, and esters. Anhydrous perchloric acid is a dangerous substance because it interacts with oxidizable matter to cause violent explosions. With proper precautions, especially the avoidance of evaporation of alcoholic solutions of perchloric acid, the use of the aqueous solutions is without hazards.[3]

[2] Caley, J. Am. Chem. Soc. **54**, 3240, 4112 (1932); **55**, 3947 (1933) Caley and Burford, Ind. Eng. Chem., Anal. Ed. **8**, 63 (1936).

[3] Perchloric acid, The G. F. Smith Co. Columbus, O.

III. Fusions

1. The insoluble residue remaining from an acid treatment of a substance may be brought into solution, generally, by fusion with an appropriate flux. The fusions are made in crucibles (20 ml. capacity) of silica, iron, nickel, silver, " palau " (gold-palladium 80 : 20) or platinum. Potassium bisulphate fusions may be made in silica or glass as well as in platinum; sodium carbonate fusions may be made in iron, nickel, " palau," and platinum; hydroxide or peroxide fusions may be made in iron, nickel or silver crucibles; sodium carbonate potassium nitrate fusions may be made in platinum, but hydrochloric acid should not be used in dissolving the fusion as the chlorine liberated will attack the platinum.

2. In making fusions the sample is well mixed with six to twenty times its weight of the fusion mixture and placed over a thin layer of the flux in the crucible and then covered by a lid of the same material as that of the crucible. Heat is applied cautiously until the mixture melts, the heat being raised during the action. When the melt has reached a quiet fusion and the resulting molten mass has become clear and homogeneous, the action is complete.

(*a*) A stiff platinum rod is placed in the molten mass and held in place until this has cooled sufficiently to solidify around the wire. By reheating the crucible the mass of fusion may be lifted out, cooled and together with the crucible placed in the beaker in which the subsequent treatment is made.

(*b*) The molten mass may be poured into a crucible lid of sufficient capacity and when cooled placed in the beaker together with the crucible.

(*c*) The molten mass is cooled by rotating the crucible or flask in such a way that it solidifies in a layer on the sides.

3. Water is now added to the material and the mixture heated until the mass disintegrates. The beaker is covered by a clock glass and the additional solvent now added. This may be hydrochloric or sulfuric acids, ammonium carbonate or any other appropriate solvent.

The following fluxes are commonly used—

1. *Sodium carbonate.*—Decomposes silicates of Al, Ca, Ce, Cr, etc.; halides of Ag; sulfates of Ba, Pb.
2. *Sodium and potassium carbonates.*—Silicates of Al, F, Fe, Ni, Se, Te, etc. The mixture fuses at a lower temperature than carbonate alone.
3. *Sodium carbonate with oxidizing agent,* i.e., $KClO_3$, KNO_3, Na_2O_2, ZnO, MgO.—Ores of Sb, As, Cr, Fe, Mo, V, Zr, sulfides, pyrites, etc.
4. *Sodium peroxide.*—Ores of Sb, As, Cr, Mo, Ni, V, U, Sn. Certain alloys and steel for chromium, etc.
5. *Potassium acid sulfate* (with H_2SO_4).—Ores of Al, Sb, Cu, Cr, Co, Fe, Mn, Ni, Rh, Ta, Ti, W. Steel with Cr, Mo, V and W, Th, phosphates, slags, oxides of metals of basic character. Silica remains insoluble. In a bisulfate fusion in a 250-ml. flask, 25–50 ml. of water and 10 ml. HCl are added and the mixture boiled until the cake dissolves. If any dark residue remains, the solution is decanted off and the residue again fused with additional flux. As stated in page 1334, certain refractory oxides require the addition of a reducing agent, such as carbon from a filter paper, to assist the acid sulfate flux. It is better to make two or more fusions on resulting residues remaining from an acid extraction of the melt, rather than to increase the amount of flux in the first charge.

6. *NaOH, KOH,* basic flux (with or without KF).—Oxidized Sb ore, ores of Cr, Sn, Zn, Zr. Sulfides and sulfates in sulfur determinations.
7. Other reagents.—NH_4Cl and $CaCO_3$—alkali silicates, KCN—tin oxide ore, CaO, Na_2O_2. Organic compounds for halide determination.

Reactions 1, 2, 3 may be carried out in iron, nickel or platinum crucibles, 5 in silica (*porcelain*) or platinum, 4, 6, and 7 in iron, nickel and silver.

Reagents.[4]—*Ammonium acetate,* $NH_4C_2H_3O_2$, is a very effective solvent of lead salts, especially the sulfate. It is prepared by adding strong acetic acid to strong ammonium hydroxide until the solution is just acid.

Ammonium hydroxide, NH_4OH, is a powerful solvent of chloride and bromide of silver.

Ammonium sulfide, $(NH_4)_2S$, readily dissolves the sulfides of arsenic, antimony, and tin. This reagent decomposes slowly, losing NH_3 and forming $(NH_4)_2S_2$. It should be kept in a dark cool place. To prepare the solution pass a rapid current of pure hydrogen sulfide through a solution of ammonia in a reagent bottle.

Hydrochloric acid, HCl, is a powerful solvent and when mixed with HNO_3 in the proportion (2–HCl : 1–HNO_3) it will dissolve gold and platinum due to the chlorine which is thus liberated in the nascent state.

Hydrofluoric acid, HF, is used to decompose silicates, the silica being volatilized.

Nitric acid, HNO_3, is a powerful solvent and oxidizing agent. The fuming variety is a more active oxidizer and desulfurizer.

Sulfuric acid, H_2SO_4, is a powerful solvent and is generally used in a dilute form made by mixing concentrated acid (1.84 sp.gr.) with water in the proportion 1–H_2SO_4 : 5H_2O.

Argol, $KHC_4H_4O_6$, potassium acid tartrate commercial grade, is a powerful reducing agent and also a basic flux.

Borax, cryst., $Na_2B_4O_7 \cdot 10H_2O$, is an acid flux sometimes used as a cover in place of NaCl. To dehydrate, fuse it in an iron or chalk lined clay crucible, pour the fused mass on a clean surface and pulverize when cold. Melting point, borax glass, 742° C.

Charcoal is a reducing agent and desulfurizer.

Iron, metallic, a basic flux, and desulfurizer. Nails or wire about ⅛ inch dia. generally used. Melting point above 1500° C.

Lead, metallic, a basic flux. It is also used as a collector of the precious metals in the assay of gold and silver ores. Granulated lead is used in scorification assays and sheet lead in bullion assays. Its silver content should be determined. Melting point, 327° C.

Lead flux.—Sixteen parts sodium bicarbonate, 16 parts potassium carbonate, 8 parts flour and 4 parts borax glass. This mixture serves as a flux, reducing agent, and desulfurizing agent.

Litharge, PbO, is a basic flux and an oxidizing and desulfurizing agent. Its silver content should be determined. Melting point, 884° C.

Silica, SiO_2, is an acid flux. Powdered lime-glass can be used as a substitute. Melting point, SiO_2, 1775° C.

[4] W. J. Crook, Lefax, Philadelphia

Potassium bisulfate, $KHSO_4$, is a decomposing agent and an acid flux. Silica is not made soluble by this reagent. Melting point, 200° C., K_2SO_4, 1072° C.

Potassium carbonate, K_2CO_3, acts same as Na_2CO_3 and is frequently mixed with it. A mixture in proportion to the molecular weights of the two substances is an excellent flux for decomposing certain silicates, clays, etc., which are difficult to handle by either carbonate alone. Melting point, K_2CO_3, 909° C.

Potassium cyanide, KCN, is a powerful reducing and desulfurizing flux and is frequently used in the fire assay of Pb, Sn, Bi and Sb. Its solution is a solvent of gold and silver. Fuses at red heat.

Potassium hydroxide, KOH, acts same as NaOH and is used for the same purposes. Melting point, 360° C.

Potassium nitrate, KNO_3, is a basic flux and also a powerful oxidizing agent. Melting point, 339° C.

Sodium bicarbonate, $NaHCO_3$, is a desulfurizing agent, a basic flux and sometimes an oxidizing agent. The corresponding potassium salt may also be used.

Sodium carbonate, Na_2CO_3, is used alone or in conjunction with other reagents for the decomposition of silicates, etc. Melting point, 849° C.

Sodium chloride, NaCl, a neutral flux, used as a cover in assay. Melting point, 804° C.

Sodium hydrate, NaOH, is used principally for the decomposition of sulfides and sulfates in sulfur determinations. Sometimes used to decompose certain silicates, oxides and certain organic compounds. It is a basic flux. Melting point of NaOH, 318° C.

Sodium nitrate, $NaNO_3$, is a decomposing and also an oxidizing agent. KNO_3 is also used for same purpose. Melting point, 316° C.

Sodium thiosulfate solution, $Na_2S_2O_3$, is a solvent for AgCl.

Oxidizing Agents.—Those in most general use are oxygen, chlorine, bromine, potassium permanganate, potassium bichromate, nitric acid, potassium chlorate, sodium nitrate, hydrogen peroxide and ammonium nitrate.

Reducing Agents.—Hydrogen, H, is used in the form of a gas which should be dry and free from impurities. Hydrogen sulfide, H_2S, is prepared by adding dilute H_2SO_4 to pure iron sulfide. If pure iron sulfide is not at hand, it can be prepared by fusing iron nails with sulfur in the proportion of about 1 part iron to 2 parts sulfur, by weight. Sodium sulfite, Na_2SO_3, is used for the reduction of ferric solutions. It separates arsenious sulfide, which is soluble in it, from the sulfides of antimony and tin, which are insoluble in it. Stannous chloride, $SnCl_2$, is frequently used for reducing iron solutions. Solutions of sugar, tartaric acid and many other organic compounds will serve as reducing agents.

THE DETERMINATION OF MOISTURE, WATER OF CRYSTALLIZATION AND WATER OF CONSTITUTION

1. Method of Loss in Weight.—A suitable weighed sample which may range from a few tenths of a gram up to 100 g. depending on the nature of the material is either heated at a suitable temperature (usually 100–105° C.)

cooled in a desiccator and weighed, or else allowed to stand, with weighing after stated intervals, over a suitable drying agent such as anhydrous magnesium perchlorate, P_2O_5, sulfuric acid (conc.), $CaSO_4$, $CaCl_2$ and the like, until the weight of the residue is constant. The percentage loss in weight is calculated. Details vary from substance to substance; the reader is therefore referred to the detailed table of contents for the determination of water in various materials, as for example, paper, soap, various ores, etc.

With crystallized salts, a temperature of 100–105° C. is frequently insufficient to drive off all of the water of crystallization. For example: Crystallized copper sulfate loses 4/5ths of its water of crystallization at 120–125° C. and the remaining 1/5 only at 240–250° C. at atmospheric pressure and humidity. Some salts melt in their own water of crystallization and undergo hydrolysis after which it may be impossible to complete the drying without decomposing the salt; this is true of common (potash) alum. In such instances the bulk of the water must be driven off at room temperature or at somewhat higher temperature, after which the drying may frequently be completed at 100° C.

Some salts, notably acid salts, like $Na_2HPO_4 \cdot 12H_2O$ lose their water of crystallization at 100° C. or below. Upon igniting the dehydrated residue at full burner temperature the salt is transformed into a "pyro" salt with loss of "water of constitution." Example: $2Na_2HPO_4 = H_2O + Na_4P_2O_7$. This is one of the kinds of changes that make it difficult in many cases to interpret fully the significance of loss on ignition at high temperatures. Oxidation of the lower oxides in the non-volatile residue is another complication that frequently occurs. For these reasons the direct determination of moisture or water of combination is frequently advisable whenever the simpler loss-in-weight determination can not be used.

Fig. 180. Apparatus for Determining Moisture.

2. Absorption Method.—The material is heated in a boat in a combustion tube as indicated in Fig. 180. The evolution of the water and its transmission to the absorption vessel are aided by a stream of dried gas, either air or other gas inert toward the material in question. The gas stream is dried by the *same drying agent* that is to be used for trapping the water that is evolved on heating. The drying agent is chosen according to the products that may be expected on heating the material strongly. For example, in determining moisture in a carbonate, sulfuric acid would absorb the water and not the CO_2 evolved. If ammonia were evolved, as for example in investigating double ammonium phosphates of magnesium, manganese, etc., lime would be a good absorbent for the water. The weight of water from a given weight of sample is found by weighing the absorption tube before and after the heating. Particular care must be taken to drive all of the water from the end of the combustion tube into the absorbing vessel.

The boat and combustion tube may be of any convenient material for the purpose at hand—hard glass, quartz, porcelain or platinum.

Penfield Method.—A variant of the evolution and weighing method that is frequently used in mineral analysis was devised by Penfield.[5] The rock or mineral powder is placed in a bulb of hard glass; the tube connected to the terminal bulb is widened out to form bulbs (one or two) at a distance of several centimeters from the terminal bulb. The open end of the tube is connected to a capillary tube by rubber during the heating of the powder. The water that is driven off is caused to condense by cooling the bulbs; the capillary prevents loss of water. Finally the bulb with the mineral residue is removed by sealing off the tube in a flame, and the part containing the water is weighed, and the water is then removed from it and the weight of the glass is determined.

Distillation Methods for Moisture †

In the distillation methods, the moisture is removed from the sample by the distillation by suitable means of heat of a solvent immiscible with water. The sample may or may not be soluble in the distilling medium. The distilling medium has a boiling point higher than water, is condensed, and collected with the water in a suitable trap or measuring tube. The excess of the condensed solvent is returned to the distilling vessel or is drawn off from the measuring tube.

Marcusson [1, 1a, 2] was one of the first to determine moisture by distilling the samples with a liquid immiscible with water and measuring the water in the manner used in the methods described in this chapter. The sample was introduced into the distilling flask into a measured quantity of toluene [2] or xylene.[1a] The mixture was distilled into a receiver constructed at the bottom to a calibrated narrow tube until several hundred cubic centimeters were recovered. The Dean and Stark, Bidwell and Sterling, and Kingman are some of the many variations of the method.

Some of the advantages of distillation methods over oven or hot plate methods are: the actual collection and measurement of the water present separated from other volatile constituents; little or no opportunity for oxidation such as exists in oven or hot plate methods; little or no effect due to humidity such as exists in oven or hot plate drying where the sample is cooled in a desiccator before final weighing; and the use of a larger and more representative sample.

The methods which are described are the most common of the distillation methods in use.

1. Water in Petroleum Products and Other Bituminous Materials.[3, 4, 5]—This method is essentially the method described by E. W. Dean and D. D. Stark.[6] The paper contains a comprehensive bibliography on moisture methods, particularly those of the distillation type.

"The method is suitable for a variety of materials, but is especially applicable to petroleum, fuel oil, road oil, coal tar, water-gas tar, coke-oven tar, and other petroleum products or bituminous materials."

For distilling apparatus, either a glass flask or a metal still may be used. Glass is generally used for petroleum products and the metal still for road

[5] Penfield, Am. J. Sci. (series 3), **48**, 31 (1894).

† Compiled by Mr. C. P. Long of the Chemical Division of Procter and Gamble Co.

materials and tars. An electric heater is preferred for glass, although a gas burner may be used. A ring gas burner is used for the metal still. Dean and Stark prefer an electric heater.[6, 7]

The apparatus, made according to A. S. T. M. specifications, may be purchased from chemical apparatus supply houses. The condenser is a glass reflux type of prescribed length so arranged as to discharge the condensate in a Dean-Stark trap. The trap is 10 ml. capacity, tapered from the 2 ml. mark to 0 ml. Above 2 ml. the inside diameter is 18 to 19 mm. The part below the 2 ml. mark is calibrated in 0.1 ml. divisions.

The solvent used when testing petroleum products or bituminous materials derived from petroleum shall be gasoline, free from water, and show the following distillation range:

5% shall distill at a temperature not below 90° C. nor above 100° C.
90% shall distill below 210° C.

The solvent used when testing bituminous materials derived from coal tar, water-gas tar, etc., shall be a coal-tar naphtha or light oil and shall show the following distilling range:

98% shall distill between 120° C. and 250° C.

Procedure: For a regular Dean and Stark trap the sample size should be such that not over 10 ml. of water are collected. For samples high in moisture a longer trap may be secured or the sample size reduced. The volume of the sample is accurately measured, transferred into the distilling vessel, and mixed with 100 ml. of solvent by swirling, taking care to avoid loss of material. The solvent can best be added to the still by rinsing the graduate with several portions. The connections between the distilling vessel, condenser and trap are made with tight-fitting corks. The heat is applied and regulated so that the condensed distillate falls from the end of the condenser at the rate of 2 to 5 drops per second. The distillation should be continued at the specified rate until no water is visible on any part of the apparatus except in the bottom of the trap. A persistent ring of condensed water in the condenser tube shall be removed by increasing the distillation rate for a few minutes.

The volume of the water in the trap at room temperature is measured and calculated to the percentage of the original volume of the sample.

2. Brown-Duvel Method for Grains.—The apparatus was described in 1907 by Brown and Duvel.[8] The apparatus was patented [9] by them in order to allow free use of it by the public. The various components of the apparatus, accessories, details of operation and effect of variation in certain details are covered in a bulletin written by D. A. Coleman and E. G. Boerner.[10] Since this bulletin covers all the specifications in detail for the flasks, thermometers, and all other parts of the apparatus and accessories as well as details of the methods for various grains, it should be available before the apparatus is placed in use.

The apparatus includes a heating chamber, arranged so several samples may be handled at the same time, and a tank containing cold water through which condensing tubes pass. The various parts are fastened on a suitable frame. Gas burners are the usual source of heat.

The distilling medium is a good grade of mineral engine oil, free from water, 0.900 specific gravity, viscosity 342 to 513 seconds Saybolt at 20° C., and open cup flash point, 350° to 400° F. The fire-point should not be over 450° F. Grains are placed in the distilling flask whole, in a weighed amount specified for each grain. With the standard thermometer in a definite position in a specified quantity of oil, heating is continued until the thermometer in the oil reaches the temperature designated for the kind of grain under test. Then the flame is extinguished. The water is measured when the thermometer has dropped to 160° C. in a graduate under the small layer of oil which distills over with the water.

The endpoint, i.e., flame extinguishing temperature for the grain, is standardized or set against drying in a water-jacketed oven under standard conditions.[11]

3. Toluene-Moisture Method (Bidwell-Sterling).[1, 2]—The receiving and measuring tube used is a modification of the Dean and Stark tube. In order to increase the accuracy of the measurement of the water layer, the calibrated lower end consists of a narrow tubular portion similar to a burette calibrated in 0.1 ml. divisions. The volumes may be read to 0.01 ml. especially if a hand-lens is used. Toluene (B.P. 111° C.) is used as distilling solvent rather than xylene (B.P. approximately 140° C.) since the lower distilling temperature of the solvent apparently eliminates decomposition of many of the organic materials under investigation.

The method was tried by Bidwell and Sterling on a large variety of organic materials, such as raisins, flours, butter, dried milk, leather,[12] molasses, grass. The method is satisfactory for moisture in essential oils,[13] soaps (especially liquid and jelly soaps), glycerine,[14] soybeans, and other grains, fats, mineral oils and all sorts of mixtures and emulsions.

The receiving tubes and also complete apparatus including condensers with standard ground glass connections may be purchased from apparatus supply houses. A 250-ml. Erlenmeyer or Soxhlet flask is satisfactory for the distilling flask although the size of the flask may be increased with large sample sizes. As source of heat, electric heaters so adjusted that the heating element is enclosed and non-glowing, and Argand gas burners are satisfactory.

The toluene used should have been previously heated under a reflux condenser connected to the flask by a Bidwell-Sterling tube until surplus moisture has ceased to distill off. The receiving tube should be carefully calibrated and before using should be absolutely clean. It is advisable to clean the tubes and condenser with chromic-sulfuric acid cleaning solution followed by water and alcohol rinses and oven drying.

Procedure.—Weigh sufficient sample to give 2 to 5 gms. of water into the distilling flask. Add sufficient toluene to cover the sample completely, usually about 75 ml. Connect the receiving tube and reflux condensers. Fill the tube through the top of the condenser. Protect the side arm from the heat of the burner by a piece of asbestos board vertically suspended.

With water flowing through the condenser, heat gently to avoid foaming, continue boiling slowly at about 2 drops per second until nearly all the water has distilled over. Then increase the rate to about 4 drops per second. A boiling piece is often an advantage. For some samples Bidwell and Sterling recommend sufficient dry sand to cover the bottom of the distilling flask.

When the water has apparently all been distilled over to the receiving tube, wash down the condenser by pouring toluene in at the top. Continue distillation a short time to determine if further water distills over. If it does, repeat the washing of the condenser. Any drops of water adhering to the sides of the condenser tubing usually can be loosened by a copper wire through the top of the condenser.

Allow the receiving tube to come to room temperature or bring to a definite temperature by immersing in a bath of this temperature. Read the volume of the water. The volume of water multiplied by the specific gravity at the temperature at which the volume is read will give the weight of water in gms.

When used on glycerine or a soap high in glycerine, the distillate may be corrected for its glycerine content by separating the aqueous layer and determining the glycerine content by the bichromate method. (See Methods for Analysis of Soap.) Alcohol and acetone cause very unsatisfactory and unreliable results.

In order to prevent soaps from foaming, a carefully measured amount of concentrated hydrochloric acid in sufficient quantity to break the soap into fatty acids is very desirable. The water content of the acid must be known and proper correction made in the amount of water recovered. Soaps containing much carbonate should be handled by the xylene-sodium acetate method. Glass wool floated in the liquid will often prevent foaming without the addition of acid.

Soybeans and grains are placed in the flask whole. Distillation is continued until water ceases to come off. The toluene in the distilling flask is allowed to cool somewhat. The beans or grain are then strained out on a coffee strainer. The solvent is returned to the distilling flask while the beans are given a rinse with a small amount of petroleum ether and allowed to drain until practically free from solvent. The sample is then quickly ground in a coffee mill and returned to the distilling flask and distillation continued until water ceases to distill over.

4. Xylene Method.—Marcusson in 1904 [2] used toluene as distilling agent in a distillation method for lubricating greases. In 1905 [1, 1a] he describes a similar method for water in oils, fats, and soaps in which xylene was used as the distillation medium. In a book [18] by Marcusson (1927) on methods for analyses for fats and oils, xylene is used as distillation solvent and the procedure is essentially that described in the previous references. If soaps are present so that foaming will occur and carbonates are absent, dry oleic acid or potassium bisulfate is added.

Rogers [12] and Bidwell and Sterling [1] pointed out that many organic materials which showed definite evidence of decomposition when xylene was used, could be safely handled when toluene was used. In the soap methods,[19] a xylene method with anhydrous sodium acetate to prevent foaming is described.

The general procedure with xylene is identical with the Bidwell-Sterling procedure using toluene. The approximately 30° C. higher boiling of xylene is often an advantage on materials that do not decompose with the liberation of water at the distilling temperature and that hold the water rather tightly.

5. Kingman Method.—The method was described by W. A. Kingman.[15] The method had been used by him for several years. It differs from the other distillation methods described in this section by the use of a non-inflammable

solvent, tetrachlorethane (also called commercially acetylene tetrachloride). The solvent is heavier than water so that the former is the lower layer in the measuring receiver. The Kingman measuring tube is equipped with a stop-cock at the lower end so the solvent may be drawn off during distillation in order to keep the water from running back to the distilling flask (Fig. 181).

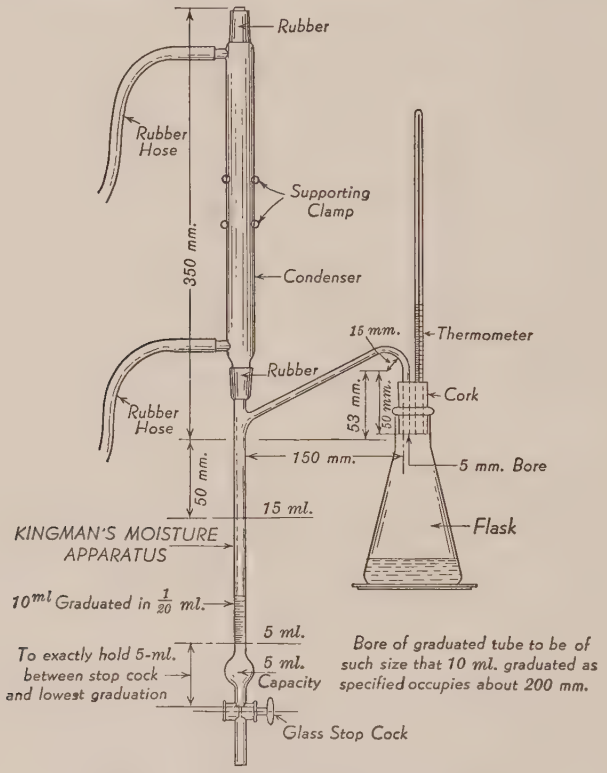

Fig. 181. Kingman Moisture Apparatus.

The method is an official method of the American Chemical Society [16] and the American Oil Chemists' Society [17] for moisture in fats.

The apparatus used is the regular Kingman set-up which may be obtained with all glass joints (Fig. 181). The distilling solvent is tetrachlorethane. Benzene is used to aid in measuring.

Determination.—Weigh from 50 to 200 gms. of the sample into a 500-ml. Erlenmeyer flask. For samples containing less than 1% moisture use 200 gms.; for samples containing from 1 to 5% moisture, 100 gms.; and for those containing larger quantities, smaller amounts. Add about 100 ml. of acetylene tetrachloride to the sample in the distillation flask and distill. Continue the distillation until from 25 to 40% of the solvent has distilled over, drawing off solvent from time to time. At first the boiling temperature will be about

80° C., rising gradually to 95–100° C., when practically all the moisture is driven off, then going up rapidly to about 144–145° C. During the rapid rise the heating should be slowed down; otherwise a too rapid evolution of vapor ensues which heats the condenser and causes the water already distilled to boil away from the receiver tube. Allow the apparatus to cool and then wash down the condenser and connecting tube into the graduated tube of the apparatus with a little coal-tar benzene. When the moisture has settled sufficiently, read the column of water, making due allowance for meniscus, and calculate the percentage.

The method is not as satisfactory for soaps as the toluene or xylene methods.

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Calculation of Percentage of Material Determined in the Original Sample to the Dry Basis, or if Determined on a Dried Sample to the Original Form Including Water. Frequently a chemist is required to report the percentage of constituent both on the dried sample and in its original form containing water. The following formulae will be of assistance in these calculations:

Let a = percentage of material found (determined on the dry basis, or in the original sample, as the case may be).
b = percentage of total dry material with water expelled.
c = per cent of water in the original sample, $100 - c = b$.

Then $\frac{100 \times a}{b}$ = per cent calculated from wet basis to dry.

$\frac{a \times b}{100}$ = per cent calculated from dry basis to wet.

DETERMINATION OF MOISTURE IN GASES

The gas to be tested is passed through a dehydrating agent such as phosphorus pentoxide, P_2O_5, alumina, Al_2O_3, or lime, CaO, contained in a weighed U-tube. The following facts should be borne in mind in selecting the dehydrating agent: (*a*) It should not absorb the gas; (*b*) it should not react chemically with the gas. For example, lime or alumina could not be used for determining moisture in sulfur dioxide, nor could phosphorus pentoxide be used in determining moisture in ammonia. For the former, phosphorus pentoxide is best, and for the latter, lime. Alumina that has been carefully heated to 1400° is useful for determining moisture in neutral gases. It should be remembered that gases dried over calcium chloride will give up moisture to concentrated sulfuric acid, and these in turn will give up moisture to phosphorus pentoxide: Professor Morley has even determined the amount of moisture that is left after this latter treatment.

Procedure. The volume of the gases required for the test varies widely according to the percentage of moisture in the gas, 1000 ml. to 10,000 ml. are generally required. For minute amounts of moisture it may be necessary to lead the gas over the dehydrating agent for a given length of time, using a manometer or difference gauge, or a gas meter. The absorption tube is weighed before and after the test and the increase in weight taken as the moisture content of the gas. See Chapter on Gas Analysis.

ALLOYS, I

ANALYSIS OF NON-FERROUS ALLOYS [1]

Classification of Alloys.—There is wide diversification among alloys commonly used, both in properties and in composition. In general, they may be divided into two groups, ferrous (containing iron) and non-ferrous (not containing iron). The great majority of alloys are non-ferrous. Those that do contain iron are called "iron alloys," to distinguish them from steel. Most of these latter are corrosion-resisting, heat-resisting and electrical resistance alloys, and resemble alloys that are strictly non-ferrous.

Alloys are utilized for various purposes requiring for instance:—mechanical strength, fatigue, resistance, corrosion resistance, electrical conductivity, lightness, heaviness, toughness, fusibility, infusibility, anti-frictional properties, etc. Naturally, one alloy cannot meet all such requirements physically, and care must also be exercised in the selection of alloys for economic reasons.

Many alloys are known to the trade by names [2] which designate their prime use in industry; others are otherwise designated. Some alloys of dissimilar composition may be put to the same purpose, while alloys of similar composition may be unsuited for a common use. Again, the same alloy may be put to several purposes. Hence it is apparent that a classification based upon the trade name of an alloy or upon the purpose to which the alloy may be put would cause considerable confusion.

The following classification is adopted from W. Campbell: [3]

Brasses	Magnesium alloys	Resistance alloys
Bronzes	Tin base alloys	Heat resistance alloys
Copper-nickel alloys	Lead base alloys	Corrosion-resistance alloys
Copper-nickel-zinc alloys	Zinc base alloys	Stainless and corrosion resistance alloys
Aluminum bronzes	Fusible metals	
Copper-manganese alloys	Gold alloys	Cobalt alloys
Copper-silicon alloys	Silver alloys	Hard alloys
Aluminum alloys	Platinum alloys	Pyrophoric alloys

Preliminary Examination.—No single reagent will act as a common solvent for all alloys. Among the solvents used may be mentioned nitric acid, hydrochloric acid, sulfuric acid, sodium hydroxide, and fusion with alkaline fluxes. At times a mixture of acids is required.

The following scheme with proper modification will serve for the identification of most alloys.

Nitric Acid Method

Treat one or more grams of the alloy filings or drillings with concentrated HNO_2 or HNO_3 (1 : 1) until the metal is completely decomposed or in solution, adding water if necessary to assist solution.

[1] Chapter contributed by W. J. Brown, Chief Analyst, National Lead Company.
[2] "Proprietary Alloys," Metal Industry, London, 1936.
[3] "A List of Alloys," by W. Campbell, published by the A. S. T. M., 1930.

(*a*) *If the metal dissolves*, antimony and tin are absent; omit their tests.

(*b*) *If the metal forms a turbid solution*, antimony and tin may be present. To a portion, add several volumes of water and boil. (*a*) If a clear solution is formed treat the entire solution in the same way, and omit tests for Sn and Sb.

(*c*) If the residue is insoluble, Sb and Sn are indicated, evaporate the entire solution to dryness, gently ignite to expel water, add HNO_3, heat, dilute and filter. If the filtrate is turbid, repeat the filtration until clear.

Precipitate.—SnO_2; $Sn_3(PO_4)_4$; Sb_2O_4; As_2O_5, all white and traces of the copper group metals.

a. Digest from 10 to 20 minutes with strong K_2S, Na_2S or $(NH_4)_2S$ solution and filter.

b. Melt with Na_2CO_3 and sulfur, cool, digest with water, and filter.

Filtrate.—Contains the H_2S group (without tin and antimony) and $(NH_4)_2S$ group.

Add from 1 to 3 ml. of concentrated H_2SO_4 and evaporate to fumes, cool, dilute and filter.

Precipitate.—Traces of copper group. If sufficient in quantity, dissolve in in HNO_3; add to filtrate containing $(NH_4)_2S$ group.

Filtrate.—Contains Sn, Sb, As, in solution. Just acidify with dilute HCl and filter.

a. Analyze the precipitated sulfides.

b. Test the filtrate for phosphates.

Precipitate.—$PbSO_4$, white. Treat with $NH_4C_2H_3O_2$ solution, filter, and add K_2CrO_4. A yellow precipitate insoluble in KOH proves lead present.

Filtrate.—Contains the H_2S group (without Sn, Sb, and Pb and free from HNO_3) and the $(NH_4)_2S$ group.

Into a portion of the solution pass in H_2S. A precipitate shows the presence of the H_2S group metals.

a. If the H_2S group is not present, as shown by a test on a portion of the solution, make a test for the $(NH_4)_2S$ group.

b. If the H_2S group is present, precipitate the metals with H_2S, filter and wash.

Precipitate—Contains the H_2S group, sulfides (without lead, tin and antimony).

If mercury is present use $(NH_4)_2S$ to separate the sub-groups.

If mercury is absent digest the precipitate with 20% KOH (2 to 3 grams dissolved in 10 ml. of water), filter and wash.

Filtrate.—Contains the $(NH_4)_2S$ group

a. Test for Phosphates. If found present consult notes on this group in Part II.

b. Make a test for the group, by making a small portion ammoniacal, and passing in H_2S, if not present. A precipitate other than sulfur indicates the presence of the metals of this group. Analyze the precipitate by the first procedure on the metals of the $(NH_4)_2S$ group.

c. If a test is made for magnesium, analyze the filtrate by procedures for the alkalies.

Precipitate.—Copper group.

Analyze by procedure outlined for the insoluble H_2S subgroup.

Filtrate.—Arsenic group in solution. Acidify, filter and analyze precipitate by the procedure for the soluble H_2S subgroup.

Methods of Procedure.—Alloys are too complex and vary too much in composition for any single method of procedure to suffice for a complete quantitative analysis. For alloys soluble in nitric acid and containing a moderate amount of tin and a small amount of antimony, the scheme for the identification of an alloy may be followed in a more or less general way. For alloys containing considerable tin or antimony, solution is best effected with a hydrochloric acid-nitric acid solution or a hydrochloric acid solution with an oxidizing agent such as potassium chlorate. Upon evaporation, lead may be separated

as chloride. Subsequent treatment will depend upon just what metals are present or desired to be determined. A procedure followed for the determination of one constituent may be unsuited for the determination of another constituent in the same alloy. Thus in a light aluminum alloy, a separation of copper, nickel, calcium and magnesium may be made by a treatment of the alloy with sodium hydroxide and these metals may be determined in the insoluble portion, while determinations for other constituents are made by dissolving the alloy in acids.

It is the exception rather than the rule that a complete analysis of an alloy containing several elements is carried out on a single weighed portion. Several determinations are made, the choice of method depending not alone upon the metals desired or the metals associated with them, but also upon the extent to which they may be present.

Difficulty of Complete Separation of Elements.—In making an exact metal analysis the chemist should have in mind that many of the separations are incomplete. Solutions may require further treatment for the recovery of unprecipitated portions and precipitates may be contaminated, thus necessitating a second and even a third separation. It is only in this manner that the accuracy of an analysis can be assured.

Limit of Accuracy.—In general an analysis is conducted in duplicate and results expressed in percentages of the alloy should not differ by more than 1 unit in the number at the right of the decimal point. This applies to components that are present in appreciable amount, say 5, 10 or more per cent. Usually a determination for a component present in such an amount is made on 1 g. of sample and results that differ by 1 unit in the tenths position represent a good percentage accuracy, whereas the same difference would represent a poor percentage accuracy when a component is present in small amount, as for example 1.0% or less. On the other hand, the same percentage accuracy is not to be expected when a minor constituent is present only to the extent of about 0.05%; in such a case duplicates as close as 0.04 and 0.05% would be satisfactory.

A metal that is a main component of one alloy may be an impurity present in very small amount in some other alloy. It is quite apparent the same method of procedure should not be followed in both instances. In order to determine a very small amount of an impurity with suitable precision a large sample would be analyzed (10 g. or more depending upon the ease of handling and the precision desired) or a more sensitive method used or both. It is a common practice in the analysis of metals to weigh out charges as large as 200 and 500 grams.

The sum of the components of an alloy should, for exact work, total within 0.2% of 100%. When, for commercial reasons, a total of 100% is expressly desired, the difference plus or minus between the summation and 100% must be proportionately taken from or added to the several components. (This, of course, is not strictly accurate, since the individual errors may vary in amount as well as in direction). Occasionally, a main constituent is obtained by difference so that the summation is exactly 100%. In reporting percentages of major components only four significant figures are retained.

Sampling.—Frequently, to save time, a busy analyst will chip a piece from an ear of a pig of metal or rasp a few grams of filings from an edge of a bar.

Most alloys are not sufficiently homogeneous to be sampled in this manner. In a molten mass of alloy there are generally constituents that have a wide range in their melting points and upon cooling, the more infusible ones solidify and attain appreciable crystal or particle size while the bulk of the mass is still liquid. If the crystals are lighter or heavier than the liquid metal, they will tend to segregate to the top or bottom. It is advisable to stir thoroughly while in a completely molten condition before casting and if the analyst is taking his own sample from a mixing pot, it should be cast in a quick-cooling form.

Samples submitted to the laboratory may be in a variety of shapes, sizes and conditions. When in the form of a pig, ingot or bar, they may be drilled, sawed or filed. Filings represent only the portion that is treated and unless the whole bar is rasped this method of sampling is to be avoided. Drillings, as a rule are too coarse for portions of 1 g. to be weighed out. However, drillings from certain low-melting alloys may be melted under rosin, and after stirring, cast into a small bar which is sampled by sawing. Sawings generally can be weighed out in 1 g. portions and this method is to be preferred for the sampling of most alloys. For the correct method of sampling see " Sampling Metals and Non-Ferrous Alloys " under chapter on Standard Methods of Sampling.

Even with correct sampling care should be exercised when weighing out the portion for analysis. In the case of a 20% antimonial lead alloy, cubic crystals of antimony form. These crystals are hard and brittle and will pulverize when cut with a hack-saw blade. Consequently, when such an alloy is sampled, the sawings obtained will be a mixture of coarse particles and fine dust. The coarse particles have an appreciably lower and the dust a very considerably higher antimony content than that of the original alloy. Sawings of this nature are screened and the fine and coarse material weighed. Each portion may then be weighed out proportionately and combined or run separately and the results calculated back to the original basis. It may be possible to weigh without screening if a large portion is weighed out, but in that event a different procedure is followed. The material is quartered down to approximately the weight desired by a riffle sampler.

Before weighing out a portion for analysis, pass a magnet through the sawings, drillings or filings to remove any iron that may have come from the cutting tool. Do not, however, pass a magnet when the alloy itself is magnetic.

ANALYSIS OF BRASSES AND BRONZES

A brass, strictly speaking, is an alloy of copper and zinc; a bronze is an alloy of copper and tin. In both alloys copper is the predominating metal. The modern brass may have other constituents in addition to copper and zinc, and the bronze other constituents in addition to copper and tin. In many bronzes the tin may be wholly displaced by another metal or metals.

Practically all of the following methods given for the analysis of a brass or a bronze call for a preliminary separation of tin as meta-stannic acid by means of solution and digestion of the alloy in nitric acid. The meta-stannic acid so obtained is subject to contamination by such alloy constituents as copper and iron and will quantitatively contain such elements as phosphorus, arsenic and vanadium provided the ratio of tin to these elements in the alloy is high enough. In addition to the above drawbacks, tin is not always quantitatively precipitated as meta-stannic acid, particularly when the alloy contains more than 0.25% of iron. In ordinary analyses of material containing but little iron, correction or provision is made for antimony and phosphorus when they are present, and the contaminants and the slight solubility losses are ignored. This procedure results in compensating errors in the determinations of copper and tin; for the impurities make up for dissolved tin while the dissolved tin plates out to a considerable extent with the copper. In umpire analyses, or with alloys high in iron or antimony, the above weaknesses of the method must be taken into account and provision must be made for the complete recovery of all tin, as well as the complete recovery of all contaminating elements carried down with the tin.[4]

ANALYSIS OF MANGANESE BRONZE (A BRASS) [5, 6]

General Considerations.—Methods are given for the determination of copper, tin, lead, iron, manganese and aluminum. Zinc is taken by difference.

For methods of determining small amounts of zinc and also nickel, phosphorus, antimony, sulfur, arsenic, see "Analysis of Bronze Bearing Metals."

DETERMINATION OF COPPER BY THE ELECTROLYTIC METHOD

Apparatus for Electrolysis. ***Electrodes.***—The electrodes recommended are of the stationary and not of the rotating type, as the stationary require less operator's time and there is less chance for erroneous results to be obtained than with the other kind. Rapid and accurate results are obtained with stationary electrodes made from platinum gauze.

Cathodes.—Platinum cathodes may be formed either from plain or perforated sheets, or from wire gauze, and may be either open or closed cylinders. They should give a depositing surface, counting both sides, of approximately 100 sq. cm. Gauze cathodes are recommended, and are best made from gauze containing approximately 400 meshes per sq. cm. (50 meshes per linear inch). The cathode should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom of the cylinder. The cylinder should be approximately 30 mm. in diameter and 30 mm. in height. The stem should be made from 1.14 mm. or 1.29 mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 135 mm., and the gauze should be sand blasted.

[4] A. S. T. M. Methods of Chemical Analysis of Metals, p. 157, December, 1936.

[5] A. S. T. M. Methods of Chemical Analysis of Metals, p. 133, December, 1936. These methods, exclusive of that for aluminum, are approved as American Standard by the American Standards Association.

[6] For Specifications for Manganese-Bronze Ingots, see 1936 Book of A. S. T. M. Standards, Part I, p. 563.

Anodes.—Platinum anodes may be of the spiral type when used in the determination of copper by electrolysis, or in the electrolytic determination of lead when it is present in amounts not over 0.2%. When used in electrolytic determination of copper and lead together in samples containing 0.2% lead or over, the anodes should be of wire gauze. Spiral anodes should be made from 1.02 mm. or 1.14 mm. wire formed into a spiral of 7 turns having a height of approximately 51 mm. and a diameter of 16 mm., the length over all being approximately 145 mm. Platinum gauze used in making anodes should contain approximately 400 meshes per sq. cm. (50 meshes per linear inch). The gauze should be formed into closed cylinders approximately 12 mm. in diameter and 30 mm. in height. The cylinders should be stiffened by doubling the gauze for about 3 mm. at the top and at the bottom. The stem should be made from 1.02 mm. or 1.29 mm. wire, flattened and welded the entire width of the gauze; the height over all should be approximately 137 mm., and the gauze should be sand blasted.

Method.—In a 150-ml. beaker dissolve 1 g. of bronze in 10 ml. of HNO_3, (sp.gr. 1.42). When the action has ceased, evaporate the solution to dryness, and bake thoroughly on the edge of a hot plate. Moisten thoroughly with HNO_3 (sp.gr. 1.42), and after digesting for a short time dilute to 50 ml. with distilled water, heat to boiling, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. Filter on double 7 cm. papers, keeping the solution hot, and receive the filtrate in a 200-ml. electrolysis beaker. Wash with boiling hot water. Add to the filtrate 5 ml. of H_2SO_4 (sp.gr. 1.84), and evaporate until copious fumes of H_2SO_4 are evolved, Dilute to about 100 ml. with distilled water, add 1.5 ml. of HNO_3 (sp.gr. 1.42). insert electrodes, cover with a pair of split watch-glasses and electrolyze. For each solution use a current density over night of 0.5 amp. per sq. dm. (4.5 amp. per sq. ft.) or use a current density of 4.0 amp. per sq. dm. (36 amp. per sq. ft.) for 2½ hours. The latter case requires the use of gauze cathodes. When the solution is colorless, wash down cover glasses, electrodes, and sides of beaker, raising the level of the liquid slightly and continue the electrolysis about 15 minutes, noting whether or not copper is deposited on the newly exposed surface of the platinum. If no copper appears, transfer about 1 ml. of the colorless solution to the cavity of a porcelain test plate, and add a few drops of fresh H_2S water. If the slightest discoloration occurs continue the electrolysis, repeating the test. Remove the cathode quickly, rinse it in distilled water and then dip it in two successive baths of alcohol. Shake off the excess alcohol and ignite the remainder by bringing it to the flame of an alcohol lamp. Keep the cathode moving continually as the alcohol burns. Weigh as metallic copper.

Accuracy.—Duplicate determinations should check within 0.10% of copper.

Notes.—1. In alloys of the type of manganese bronze, which carry considerable iron, it is impossible to remove the tin quantitatively as metastannic acid (H_2SnO_3), notwithstanding the preliminary baking. Upon testing (by the addition of H_2S water), the liquid in the pits of the test plate may be colored yellow, due to the tin present, but there should be no darkening due to the presence of copper. If the cathode appears dark, as though tin had been deposited on it, dissolve the coating in 10 ml. of HNO_3 (sp.gr. 1.42), filter off the tin as before, add to the filtrate 5 ml. of H_2SO_4 (sp.gr. 1.84), and redeposit copper by electrolysis. It is rarely necessary thus to purify the deposited copper.

2. If zinc is to be determined in the alloy be careful to keep the solution quantitative when the electrodes are removed, catching all washings in the beaker containing the electrolyte.

3. A slight amount of copper is retained by the metastannic acid (H_2SnO_3), which should be recovered in very accurate work but is generally neglected in routine analysis.

4. In the case of alloys containing larger amounts of tin and less than 0.2% of iron, a preliminary baking is not essential.

DETERMINATION OF LEAD BY THE ELECTROLYTIC METHOD

(For Samples Containing up to 0.2% of Lead)

Method.—In a 250-ml. beaker dissolve 5 g. of bronze in 25 ml. of HNO_3 (sp.gr. 1.42). Allow the solution to bake dry on the edge of a hot plate or by standing over night on the steam bath. Add 17 ml. of HNO_3 (sp.gr. 1.42), and after digesting for a short time, add 85 ml. of hot water and heat to boiling for a few minutes. Allow the solution to stand for several hours at a temperature just below the boiling point. Filter off the precipitated H_2SnO_3 on double closely woven filter papers, being careful to keep the solution hot throughout the process of filtration. Wash with boiling hot water. Receive the combined filtrate and washings in a 250-ml. beaker. Dilute to about 150 ml. with distilled water and insert electrodes. In the positive terminal use a sand-blasted platinum gauze electrode such as is used for the cathode in the determination of copper; in the negative terminal insert an electrode such as is used for the anode in the determination of copper. Cover with a pair of split watch glasses and electrolyze. For each solution use a current density of 1.25 to 1.5 amp. per sq. dm. (11.25 to 13.5 amp. per sq. ft.) for one hour. Wash down the cover glasses, electrodes and sides of beaker, raising the level of the liquid slightly, and continue the electrolysis for 15 minutes. If no darkening of the newly exposed surface of the platinum can be detected the lead has been entirely deposited. Continue the electrolysis until no darkening of the platinum can be detected when the current has been passed for 15 minutes after the level of the liquid has been raised.

When the lead has been entirely deposited, remove the anode quickly, rinse it in distilled water and then in alcohol, and dry it at 210° C. for one-half hour. Weigh as PbO_2, using the factor for lead 0.8643 instead of the theoretical value.

Accuracy.—Duplicate determinations should check within 0.01% of lead. Results obtained by this method are likely to be about 0.01% too high. For exceptionally accurate or investigation work redissolve the coating from the electrode and determine the lead as sulfate. See the " Determination of Lead as Sulfate."

Notes.—1. It is impossible to remove the tin quantitatively as H_2SnO_3 in the case of alloys containing over 0.25% of iron, and traces of tin are sometimes found in the PbO_2 deposit. Small amounts of manganese also are occasionally deposited with the PbO_2. Tin and manganese are rarely present in the PbO_2 in amounts which necessitate a purification of the deposit.

2. In this and the following method a slight amount of lead may be retained by the H_2SnO_3. This should be recovered in very accurate work, but is neglected in routine analysis.

3. See note 4 under "Determination of Copper by the Electrolytic Method."

4. See note 2 under "Determination of Lead by the Electrolytic Method, Analysis of Bronze Bearing Metal."

DETERMINATION OF LEAD AS SULFATE

(For Samples Containing up to 0.2% of Lead) (Optional)

Solutions Required. *Lead Acid.*—Mix 300 ml. of H_2SO_4 (sp.gr. 1.84), and 1800 ml. of distilled water. Dissolve 1 g. of lead acetate, c.p., in 300 ml. of distilled water and add this to the hot solution, stirring meanwhile. Let stand at least 24 hours and siphon through a thick asbestos filter.

Dilute Alcohol for Washing.—Mix equal parts of denatured alcohol and distilled water.

Method.—Proceed exactly as in "Determination of Lead by the Electrolytic Method" up to the point where the precipitated H_2SnO_3 is filtered and washed.

To the combined filtrate and washings add 120 ml. of lead acid, and evaporate until copious fumes of H_2SO_4 are evolved. Cool, add 105 ml. of distilled water to dissolve the salts and to make the acid concentration the same as in lead acid, heat to boiling, and allow to cool and settle for 5 hours, or over night if convenient. Filter on a weighed porcelain Gooch crucible and wash with lead acid. Wash out the lead acid with dilute alcohol, set the gooch crucible inside a porcelain crucible, dry and ignite for 5 minutes at the full heat of a Tirrill burner, cool and weigh as $PbSO_4$, which contains 68.33% lead.

Accuracy.—Duplicate determinations should check within 0.01% of lead. Results obtained by this method are likely to be about 0.01% too low.

Notes.—1. It is impossible to remove the tin quantitatively as H_2SnO_3 in the case of alloys containing over 0.25% of iron, but by the preliminary baking and long standing, most of the H_2SnO_3 is precipitated.

2. See Note 4 under "Determination of Lead by the Electrolytic Method."

3. For the determination of lead as a sulfate in alloys containing over 0.2% see, "Analysis of Bronze Bearing Metal."

DETERMINATION OF COPPER AND LEAD SIMULTANEOUSLY

(For Samples Containing over 0.2% of Lead)

Method.—In a 150-ml. beaker, dissolve 1 g. of brass in 10 ml. of HNO_3 (sp.gr. 1.42). When the action has ceased, evaporate the solution to dryness, and bake thoroughly on the edge of a hot plate. Add 10 ml. of HNO_3 (sp.gr. 1.42), and after digesting for a short time add 50 ml. of hot distilled water, heat to boiling, and allow to stand and settle for about one hour, keeping the temperature just below the boiling point. Filter on double 7 cm. filter paper, keeping the solution hot, and receive the filtrate in a 200-ml. electrolysis beaker. Wash with boiling water, dilute to about 100 ml. and insert electrodes. In the positive terminal insert one of the platinum gauze anodes previously described, and in the negative terminal insert a platinum gauze cathode. Cover with a pair of split watch glasses and electrolyze. For each solution use a current density of 3 to 5 amp. per sq. dm. (27 to 45 amp. per sq. ft.). After about 45 minutes, the lead will have been entirely deposited on the anode as PbO_2; without interrupting the current add to the electrolyte 3 to 4 ml. of H_2SO_4 (sp.gr. 1.84), and continue the electrolysis. When the solution is colorless, wash down the cover glasses, electrodes and sides of the beaker, raising the level of the liquid slightly, and continue the passage of the current for

about 15 minutes, noting whether or not copper is deposited on the newly exposed surface of the platinum. If no copper appears, transfer about 1 ml. of the colorless solution to the cavity of a porcelain test plate, and add a few drops of fresh H_2S water. If the slightest discoloration occurs, continue the electrolysis until there is no discoloration whatever upon repeating the test. Remove the solution from the electrodes quickly without interrupting the current. Rinse the electrodes in distilled water and then dip them in two successive baths of alcohol. Dry the anode at 210° C. for 30 minutes. Weigh as PbO_2, using the factor for lead 0.8643 instead of the theoretical value. Shake off the excess alcohol from the cathode and ignite the remainder by bringing it to the flame of an alcohol lamp. Keep the cathode moving continually while the alcohol burns. Weigh as metallic copper.

Accuracy.—Duplicate copper determinations should check within 0.10% of copper. Duplicate lead determinations should check within 0.02% of lead. Lead results obtained by this method are likely to be about 0.01% too high. See notes under the " Determination of Lead by the Electrolytic Method."

DETERMINATION OF TIN

Solutions Required. *Dilute Hydrochloric Acid.*—Mix 500 ml. of HCl (sp.gr. 1.18), and 500 ml. of distilled water.

Dilute Sulfuric Acid.—Mix 300 ml. of H_2SO_4 (sp.gr. 1.84), and 600 ml. of distilled water.

Dilute Ammonia.—Mix 100 ml. of NH_4OH (sp.gr. 0.90), and 900 ml. of distilled water.

Ammonium Acetate Solution for Washing.—Dissolve 10 g. of ammonium acetate in 300 ml. of distilled water. Make slightly acid with acetic acid and saturate with H_2S gas.

Method.—In a 150-ml. beaker dissolve 2 g. of bronze in a mixture of 10 ml. of HCl (sp.gr. 1.18), and 5 ml. of HNO_3 (sp.gr. 1.42). Dilute to about 75 ml. with distilled water. Add NH_4OH (sp.gr. 0.90), until the basic salts of copper have dissolved and the solution has become a deep blue. Boil and allow to settle, and filter on a closely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl. Dilute the solution to about 100 ml. Add NH_4OH (sp.gr. 0.90) until a permanent precipitate forms. Heat the solution to boiling, allow to settle, filter and wash as before. Dissolve the precipitate on the filter with boiling hot dilute H_2SO_4, washing the paper very thoroughly with this acid. Add NH_4OH (sp.gr. 0.90) cautiously until the precipitate which forms at first dissolves rather slowly. Allow the solution to stand for some hours and if any lead sulfate forms filter it off. Dilute the solution to about 200 ml. and saturate it with H_2S gas. Filter the precipitated tin sulfide off on double papers and wash with ammonium acetate solution, retaining the filtrate and washings for the iron determination. Dry the precipitate and place it with the papers in a porcelain crucible which projects part way through a hole in a piece of asbestos board. Heat slowly until any free sulfur has been driven off, but without allowing the sulfur to burn. When the sulfur has been expelled, place the crucible on a triangle and ignite slowly at first and finally at the full heat of the

burner. If the precipitate weighs more than 20 mg. heat to constant weight, using a blast lamp Weigh as SnO_2, which contains 78.77% of tin.

Accuracy.—Duplicate determinations should check within 0.06% of tin.

NOTES.—1. If, during ignition, the sulfur is allowed to burn, some tin sulfate may be formed, causing high results. On the other hand, low results may be caused by too high heat, which causes spattering and volatilizes some tin sulfide.

2. Tin and iron are best determined on the same sample, retaining the filtrate from the tin sulfide precipitate to use for the iron determination.

3. For the determination of tin in alloys containing more tin than is present in this alloy see "Analysis of Bronze Bearing Metal."

4. In alloys containing an appreciable amount of antimony and in the presence of a large excess of tin, the antimony as determined by the method given under "Analysis of Bronze Bearing Metal" should be calculated to Sb_2O_4 and a corresponding amount deducted from the weight of the ignited SnO_2 before calculating to tin. Similarly arsenic found in the alloy should be calculated to As_2O_5 and a corresponding correction made.

DETERMINATION OF IRON

Solutions Required.—See "Determination of Tin," and the following:

Dilute Sulfuric Acid for Reductor.—Mix 50 ml. of H_2SO_4 (sp.gr. 1.84), and 1000 ml. of distilled water. This solution is used boiling hot.

Potassium Permanganate.—Dissolve 0.2 g. of $KMnO_4$ in water, filter through asbestos, and dilute to 1000 ml. with distilled water. Standardize against 0.020 g. portions of pure sodium oxalate. Each milliliter is equivalent to approximately 0.00033 g. of iron.

Method.—Proceed exactly as in the "Determination of Tin" through the filtration and washing of the precipitated tin sulfide. Combine the filtrate and washings from the tin sulfide precipitate and boil until all H_2S is expelled. Add HNO_3 (sp.gr. 1 42) until the iron is oxidized, which is shown by the solution becoming clear and of a yellowish color. Add about 5 g. of NH_4Cl, then NH_4OH (sp.gr. 0.90) until a permanent precipitate forms. Boil, allow to settle, filter on a loosely woven filter paper and wash with dilute ammonia and with hot water. Dissolve the precipitate on the paper with hot dilute HCl and add NH_4OH (sp.gr. 0.90) to the solution again until a permanent precipitate forms. Boil, allow to settle, filter on a loosely woven filter paper, and wash with dilute ammonia and with hot water until all NH_4Cl is removed. Dissolve the precipitate and wash the filter paper with 100 ml. of dilute H_2SO_4 for reductor. Pass the solution through a Jones reductor, wash first with 150 ml. of the H_2SO_4 for reductor and then with 100 ml. of distilled water. Titrate with the standard $KMnO_4$ solution.

Accuracy.—Duplicate determinations should check within 0.03% of iron.

NOTES.—1. A blank determination should be made on corresponding amounts of acid and water passed through the reductor and the results should be corrected accordingly. About 0.5 ml. of the permanganate will be required to give a permanent coloration to the solution.

2. A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the body of the reductor.

3. A description and further details of use of reductor see "Estimation by Reduction with Jones Reductor and Oxidation by Standard Permanganate Solution" and "Notes on Reductor Technique" in chapter under Molybdenum.

4. For the determination of iron in alloys containing more tin than is present in this alloy see "Analysis of Bronze Bearing Metal."

DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD

Solutions Required.—*Solution for Dissolving.* Mix 500 ml. of H_2SO_4 (sp.gr. 1.84), 200 ml. of HNO_3 (sp.gr. 1.42) and 1700 ml. of distilled water.

Silver Nitrate.—Dissolve 1.33 g. of $AgNO_3$ in 1000 ml. of distilled water.

Stock Sodium Arsenite Solution.—To 15 g. of arsenious oxide (As_2O_3) in a 300-ml. Erlenmeyer flask add 45 g. of Na_2CO_3 and 150 ml. of distilled water. Heat the flask and contents on the steam bath until the As_2O_3 is dissolved. Cool the solution, filter and make up to 1000 ml. with distilled water.

Standard Sodium Arsenite Solution.—Mix 200 ml. of the stock sodium arsenite solution with 2500 ml. of distilled water, and standardize against a steel or iron of known manganese content as determined by the Bismuthate Method, or standardize against one of the Bureau of Standards' standard irons or steels. One milliliter of this solution should be equivalent to approximately 0.00035 g. of manganese.

Ammonium Persulfate.—Dissolve 6 g. of ammonium persulfate in 100 ml. of distilled water. (This solution should be made up as needed as it deteriorates rapidly.)

Method.—Adjust the size of the sample to the expected percentage so that the portion taken does not contain more than 0.002 g. of manganese. Place it in a 250-ml. Erlenmeyer flask with 24 ml. of the "solution for dissolving" and heat until solution is complete. Boil until the oxides of nitrogen are expelled. Dilute to 100 ml. with boiling hot water, add 20 ml. of $AgNO_3$ solution and 30 ml. of the persulfate solution, then remove to a moderately warm place to stand for a few minutes for complete development of the permanganic acid. Cool to below 25° C., and titrate with the standard arsenite solution to the disappearance of the pink color.

Accuracy.—Duplicate determinations should check within 0.02% of manganese.

Notes.—1. Large amounts of permanganic acid are unstable; on that account samples which contain large amounts of manganese should have correspondingly small samples weighed out. For instance, with metal containing 1.5% of manganese use a 0.10 g. sample, while if metal contains 0.75% manganese use a 0.20 g. sample.

2. The solution must be cold when it is titrated, for high temperatures cause low results to be obtained.

DETERMINATION OF MANGANESE BY THE BISMUTHATE METHOD (OPTIONAL)

Solutions Required. *Nitric Acid (1 : 3).*—Mix 250 ml. of HNO_3 (sp.gr. 1.42). and 750 ml. of distilled water.

Nitric Acid for Washing.—Mix 30 ml. of HNO_3 (sp.gr. 1.42), and 970 ml. of distilled water.

Ferrous Ammonium Sulfate.—Dissolve 12.4 g. of ferrous ammonium sulfate crystals in 950 ml. of distilled water, and add 50 ml of H_2SO_4 (sp.gr. 1.84).

Potassium Permanganate.—Dissolve 1 g. of $KMnO_4$ in 1000 ml. of distilled water. Allow it to stand for about one week and then filter it through asbestos. Standardize against 0.10 g. portions of pure sodium oxalate.

Method.—In a 250-ml. Erlenmeyer flask dissolve 1 g. of bronze in 50 ml. of HNO_3 (1 : 3). Without filtering off the H_2SnO_3, cool and add 0.5 g. of sodium bismuthate. Heat for a few minutes until the purple color has disappeared, with or without the precipitation of manganese dioxide. Add a little ferrous-ammonium sulfate solution until the solution becomes clear, and boil until the oxides of nitrogen are expelled. Cool, add an excess of sodium bismuthate and agitate for a few minutes. Add 50 ml. of HNO_3 for washing and filter through an alundum crucible or an asbestos pad. Wash with 50 ml. of the HNO_3 for washing. Add from a pipette or a burette 10 ml. of ferrous-ammonium sulfate solution and titrate with $KMnO_4$. Owing to the presence of considerable copper, the end point is somewhat different from the normal pink color.

In exactly the same manner carry through a blank determination, using the same amounts of HNO_3 and sodium bismuthate as was done with the regular sample. Finally add exactly 10 ml. of ferrous-ammonium sulfate solution and titrate with $KMnO_4$. The difference between the two titrations is due to the manganese. Since one manganese as permanganate oxidized five irons, the iron value of the permanganate multiplied by the factor (Mn/5Fe) (or 0.1967) gives the value in terms of manganese.

Accuracy.—Duplicate determinations should check within 0.02% of manganese.

Notes.—1. Instead of employing the method of reducing the permanganic acid by means of standardized ferrous ammonium sulfate solution and titrating the excess of this reagent, it is possible to reduce the permanganic acid by standard sodium arsenite solution. See "Determination of Manganese by the Persulfate Method."

2. The filtrate from the bismuthate must be perfectly clear, as the least particle of bismuthate carried into the filtrate will vitiate the results.

DETERMINATION OF ALUMINUM IN SMALL QUANTITIES[7]

(a) General Method for Accurate Work

Solutions Required. *"Electrolytic Solution."*—Mix 300 ml. of HNO_3 (sp.gr. 1.42), 1700 ml. of distilled water and 500 ml. of H_2SO_4 (sp.gr. 1.84).

Acidified H_2S Solution for Washing.—Dilute 10 ml. of HCl (sp.gr. 1.18) with 1000 ml. of distilled water and saturate with H_2S.

Phenylhydrazine Solution for Washing.—Add saturated SO_2 water to a few ml. of phenylhydrazine until the crystalline sulfite first formed redissolves and then add phenylhydrazine drop by drop with vigorous agitation until the odor of SO_2 is no longer perceptible; dilute 5–10 ml. of this solution with 100 ml. of hot water and allow to remain at the boiling point for a few minutes to get rid of the excess SO_2.

2% NH_4Cl Solution for Washing.—Mix 30 ml. of HCl (sp.gr. 1.18) with 200 ml. of distilled water, add methyl red, neutralize with NH_4OH until the solution changes to a distinct yellow and then dilute to 1000 ml. with water.

Method.—Dissolve 1 g. of the brass or bronze in 35 ml. of "electrolytic solution," dilute with 100 ml. of distilled water and remove copper by electrolysis. Evaporate the electrolyte to fumes of SO_3. (If much tin is present,

[7] A. S. T. M. Methods of Chemical Analysis of Metals, p. 170, December, 1936.

boil the sulfuric acid solution vigorously for a few minutes.) Cool and dilute with 100 ml. of water. Filter off the $PbSO_4$ and any tin that may be precipitated at this point, washing with hot water. Dilute the filtrate to at least 200 ml.

Pass H_2S into the filtrate for 30 minutes. This will precipitate any copper, lead, tin, arsenic or antimony which may be present. Allow the sulfides to settle and filter, washing with acidified H_2S water. Boil the filtrate to one-half volume to expel H_2S, add 3 ml. HNO_3 (sp.gr. 1.42) and boil for a few minutes to oxidize the iron.

Precipitate the iron and aluminum according to the following (Blum, J. Am. Chem. Soc., **38**, 1282, 1916). Add 10 ml. of HCl (sp.gr. 1.18) and just neutralize with NH_4OH, using methyl red as indicator. Boil for two minutes and filter, washing with hot 2% NH_4Cl. Dissolve the precipitate from the paper with boiling hot HCl (1 : 1) and wash alternately with hot water and HCl (1 : 1) into the beaker in which the precipitation was made. Reprecipitate the iron and aluminum following the same procedure as before.

Dissolve the precipitate again with hot HCl (1 : 1), dilute to 100 ml. with water, make just ammoniacal, then only add acid enough to hold iron in solution. Add sufficient saturated solution of ammonium bisulfite to reduce the iron (5 to 20 drops). Add a few drops of methyl orange, quickly bring to neutrality with NH_4OH and then add 6 to 7 drops of HCl (1 : 1) in excess. Finally add from 1 to 3 ml. of phenylhydrazine and stir until the precipitate becomes flaky. The supernatant liquor should be plainly acid to litmus and the precipitate may be colored owing to organic matter. Filter and wash with phenylhydrazine wash solution. Ignite in a weighed platinum crucible, finishing with the blast for five minutes. Weigh as Al_2O_3. The weighing should be made rapidly and with the crucible covered as Al_2O_3 is somewhat hygroscopic.

Notes.—1. For small amounts of aluminum a 5 g. sample should be used. In this case dissolve in 60 ml. of "assay solution" of the following proportions: 7 vols. HNO_3 (sp.gr. 1.42), 10 vols. H_2SO_4 (sp.gr. 1.84), 25 vols. H_2O.

2. When phosphorus is present, the final precipitate will be Al_2O_3 plus P_2O_5. In this case it is necessary to fuse the residue with Na_2CO_3, dissolve with hot water, acidify with HNO_3 and determine phosphorus by the alkalimetric method. The phosphorus is calculated to P_2O_5 and subtracted.

3. For accurate work the Al_2O_3 residue is treated with HF and H_2SO_4 for the removal of possible SiO_2.

4. Ammonium bisulfite solution may be prepared by saturating cold NH_4OH (1 : 1) with SO_2 until yellow.

5. This method is especially satisfactory for small amounts of aluminum in brass or bronze since no reagents are used which may contaminate the precipitate with aluminum, iron or silica. A precipitate with phenylhydrazine gives positive indication of the presence of aluminum.

(b) Rapid Method for Control Work

Solutions Required. *2.5% Sodium Hydroxide Solution.*—Dissolve 25 g. NaOH (free from aluminum) in 1000 ml. water.

Sodium Sulfide Solution.—Dissolve 150 g. NaOH (free from aluminum) in 1000 ml. of water, saturate 500 ml. of this solution with H_2S and mix the remaining 500 ml. of solution with it.

Dilute Hydrochloric Acid (1 : 3).—Mix 200 ml. of HCl (sp.gr. 1.18) with 600 ml. of water.

Acidified H_2S Water.—Dilute 10 ml. of HCl (sp.gr. 1.18) with 1000 ml. of water and saturate the solution with H_2S.

2% NH_4Cl Solution.—Mix 30 ml. of HCl (sp.gr. 1.18) with 200 ml. of water, add methyl red, neutralize with ammonia until the solution changes to a distinct yellow and then dilute to 1000 ml. with water.

Method.—Dissolve 2 g. of the sample in 20 ml. of HCl (sp.gr. 1.18) and 5 ml. of HNO_3 (sp.gr. 1.42). Boil the solution to expel chlorine and dilute with 50 ml. of water. Nearly neutralize the cold solution with 2.5% NaOH solution (or stronger if much free acid is present) and pour it slowly with constant shaking into a 500-ml. volumetric flask containing 100 ml. of sodium sulfide solution. Dilute to the mark with 2.5% NaOH solution and mix thoroughly. Filter on a large, dry, No. 42 Whatman filter paper or its equivalent and keep the paper well filled with the solution lest iron be oxidized and dissolved. Reject the first 20–25 ml. and catch exactly 250 ml. which will represent 1 g. of sample. In routine analysis of material containing not more than 1% of aluminum the aliquot portion may be gathered in a 250-ml. graduate.

Transfer the aliquot portion to a 600-ml. beaker, neutralize the solution with dilute HCl (1 : 3) and finally add 25 ml. excess. Digest at 40–60° C. for one hour and filter and wash the paper and precipitate with acidified H_2S water.

Boil the filtrate and washings to expel H_2S, add a few drops of methyl red indicator and then dilute ammonia (1 : 2) until the solution is just distinctly yellow. Boil for two minutes and filter at once through a small filter. Wash the beaker, paper and precipitate two or three times with hot 2% NH_4Cl solution and discard the filtrate. Dissolve the precipitate in 20 ml. of hot dilute HCl (1 : 3), wash the filter thoroughly with small portions of water and reserve it for the second filtration. Dilute the filtrate to 50 ml., add methyl red and precipitate with dilute ammonia as before. Filter, wash with hot 2% NH_4Cl solution and ignite and weigh.

The ignited residue is prone to carry SiO_2 and must be purified before weighing as follows. Add one or two drops of water, one drop of diluted H_2SO_4 and 1 to 5 ml. HF. Evaporate to dryness, increase the heat slowly and finally heat with a blast lamp or its equivalent. Weigh as Al_2O_3. The weight of Al_2O_3 corrected for the blank and multiplied by 52.91 gives the per cent of aluminum.

Notes.—The first $Al(OH)_3$ precipitate will carry down some NaCl and much of any silica that was dissolved in the NaOH solution; hence it is not safe to omit the second precipitation and HF treatment. There is no attack on the glassware during the short contact with the weak cool alkaline solution. It is, of course, preferable that the NaOH be free from aluminum. The most satisfactory test for it lies in running an analysis with non-ferrous alloys containing no Al. Direct test, by acidification followed by precipitation with ammonia is sufficient if no precipitate is obtained, but is of doubtful value in case one appears, for it may contain other elements, such as iron, which do not affect the results.

If phosphorus is known to be present the method should be followed through the first addition of ammonia. If aluminum is indicated, re-acidify the solution with HCl, add macerated paper, two drops of methyl orange and 10 ml. of a solution of diammonium

phosphate (10%). Render the solution just ammoniacal, then just restore the pink color with dilute HCl (1 : 3), heat to boiling and add 30 ml. of 25% ammonium acetate. Boil for five minutes, filter on an 11 cm. No. 42 Whatman paper and wash with hot 5% NH_4NO_3 solution until 5 ml. of the washings no longer give a test for chlorides. Ignite in platinum or porcelain, heat at about 1100° C. for 10 minutes and weigh as $AlPO_4$. This method is not strictly accurate on account of the uncertain composition of the phosphate but is sufficiently accurate for all but the most painstaking analyses.

ANALYSIS OF BRONZE BEARING METALS [8]

General Considerations.—The determinations given below cover most of the constituents commonly found in a bronze.

For the determination of manganese and aluminum see " Analysis of Manganese Bronze."

DETERMINATION OF COPPER BY THE ELECTROLYTIC METHOD

Method.—In a 150-ml. beaker, dissolve 1 g. of the bronze in 10 ml. of HNO_3 (sp.gr. 1.42). When the action has ceased, boil until the oxides of nitrogen are expelled, add 50 ml. of hot distilled water and proceed as in " Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

Retain the papers containing the precipitate of H_2SnO_3 for subsequent use in the tin determination.

Notes.—1. Copper, zinc and tin are conveniently determined on the same sample, tin being first removed, and any zinc tested for after copper has been deposited by electrolysis.

2. If the solution becomes cool during the first filtration, some of the H_2SnO_3 may dissolve.

3. See note 3 under "Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

4. For alloys containing over 0.25% of iron it is advisable to remove the tin as H_2SnO_3 by a preliminary baking. See "Determination of Copper Analysis of Manganese Bronze."

DETERMINATION OF TIN

(FOR SAMPLES FREE FROM PHOSPHORUS)

Method.—See the " Determination of Copper by the Electrolytic Method."

Use the papers containing the meta-stannic acid which was filtered off in the " Determination of Copper by the Electrolytic Method." Ignite the papers with the precipitate while moist in a porcelain or platinum crucible, slowly at first, and finally at the full heat of the burner. If the precipitate

[8] A. S. T. M. Methods of Chemical Analysis of Metals, p. 157, December, 1936.

weighs more than 20 mg., heat to constant weight, using a blast lamp. Weigh as SnO_2, and calculate to Sn.

NOTES.—1. This method is not accurate for alloys which contain phosphorus, or which contain over 0.25% of iron. See "Determination of Tin, Analysis of Manganese Bronze."

2. The ignited tin oxide contains small amounts of iron and copper as well as any phosphorus, antimony or arsenic which may be present in the alloy. Qualitative tests should be made for phosphorus, antimony and arsenic. In the absence of antimony and arsenic the following "Qualitative Test for Phosphorus" is here made use of to detect phosphorus and to estimate its amount, if any is found.

QUALITATIVE TEST FOR PHOSPHORUS

Solutions Required. *Ferric Chloride.*—Dissolve 25 g. of ferric chloride in 100 ml. of distilled water, and add 25 ml. of HCl (sp.gr. 1.18).

Method.—Dip a piece of the alloy into a few milliliters of ferric chloride for about ten seconds, and rinse it in running water. Alloys containing phosphorus are darkened noticeably where they have been dipped; alloys containing over 0.25% of phosphorus are rendered almost black by this test.

In alloys containing up to 0.20% of phosphorus, a correction for its presence in the ignited tin oxide may be made according to the following empirical method. From the phosphorus content of the alloy, which has been determined on a separate sample, calculate the weight of P_2O_5 and subtract two-thirds of this weight from the weight of the ignited tin oxide containing phosphorus. The remainder is considered as pure SnO_2. The factor for converting phosphorus to $\frac{2}{3} \times P_2O_5$ is 152.6%, or approximately 1½ times the phosphorus content of the sample.

If the alloy contains over 0.20% of phosphorus, a special method for the determination of tin should be used.

In alloys which contain over 0.25% of iron, use the method for the "Determination of Tin, Analysis of Manganese Bronze."

DETERMINATION OF TIN FOR SAMPLES CONTAINING PHOSPHORUS

Solutions Required. *Yellow Ammonium Sulfide.*—Saturate 150 ml. of NH_4OH (sp.gr. 0.90) with H_2S gas, and then add 50 ml. more of NH_4OH. Dissolve in this solution 3 or 4 g. of sulfur flour, and about 1 g. of NH_4Cl. Make up this solution fresh, and filter immediately before using.

Dilute Yellow Ammonium Sulfide for Washing.—Mix 20 ml. of yellow ammonium sulfide, prepared as above, and 400 ml. of distilled water.

Ammonium Acetate for Washing.—Dissolve 10 g. of ammonium acetate in 300 ml. of distilled water, make slightly acid with acetic acid and saturate with H_2S gas.

Method.—See the "Determination of Copper by the Electrolytic Method."

Use the papers containing the freshly filtered meta-stannic acid which was filtered off in the "Determination of Copper by the Electrolytic Method." Transfer the papers with the precipitate to a 150-ml. beaker, and cover with 40 to 50 ml. of yellow ammonium sulfide. Warm for about 15 minutes, or

until the meta-stannic acid has dissolved. Filter and wash thoroughly with dilute yellow ammonium sulfide. Acidify the combined filtrate and washings cautiously with 50% acetic acid. Warm, and allow the precipitated tin sulfide and sulfur to settle. Filter on double papers and wash with ammonium acetate solution. Dry the precipitate, and proceed exactly as in " Determination of Tin, Analysis of Manganese Bronze."

NOTES.—1. The ignited tin oxide will contain any arsenic or antimony that was present in the sample. For its correction see Note 4, "Determination of Tin," Analysis of Manganese Bronze.

2. In the case of alloys containing smaller amounts of tin and over 0.25% of iron proceed as in "Determination of Tin, Analysis of Manganese Bronze."

DETERMINATION OF LEAD BY THE ELECTROLYTIC METHOD

Method.—Proceed exactly as in " Determination of Copper by the Electrolytic Method " up to the point where the tin has been separated as H_2SnO_3.

To the filtrate add 9 ml. of HNO_3 (sp.gr. 1.42), dilute to a volume of about 150 ml. and electrolyze for 2 hours, using a current of 2 amperes. See " Determination of Lead by the Electrolytic Method, Analysis of Manganese Bronze."

NOTES.—1. See Notes 1 and 2 under "Determination of Lead by the Electrolytic Method, Analysis of Manganese Bronze."

2. *Samples for Analysis.*—When lead is less than 0.10%, a 5 or 10 g. sample is taken. The 5 g. sample should be dissolved in 25 ml. of HNO_3. The 10 g. sample should be dissolved in 45 ml. of HNO_3. When the lead content is greater than 15% dissolve the sample in HNO_3 as described under Method, transfer the solution to a graduated flask and choose aliquot portions for analysis in order not to exceed the above mentioned limit of lead to be deposited on the anode as PbO_2. The lead peroxide will tend to flake off the electrode when the amount deposited becomes excessive.

DETERMINATION OF LEAD AS SULFATE (OPTIONAL)

Solutions Required.—See " Determination of Lead as Sulfate, Analysis of Manganese Bronze."

Method.—In a 150-ml. beaker dissolve 1 g. of bronze in 10 ml. of HNO_3 (sp.gr. 1.42). When dissolved, boil until the oxides of nitrogen are expelled, add 50 ml. of boiling water, allow to stand, filter and wash with hot water. (For further particulars see " Determination of Copper, Analysis of Manganese Bronze.")

To the filtrate add 40 ml. of lead acid and evaporate to fumes of H_2SO_4. Cool, add 35 ml. of water to dissolve the salts, heat to boiling, allow to cool and settle for 5 hours and proceed as in " Determination of Lead as Sulfate, Analysis of Manganese Bronze."

NOTES.—1. Copper and lead may be determined on the same samples if so desired. In such a case, after filtering off the lead sulfate and washing with lead acid, and before washing with dilute alcohol, remove the filtrate, add 3 ml. of HNO_3 (sp.gr. 1.42), dilute to 120 ml. and determine copper by electrolysis. See the "Determination of Copper by the Electrolytic Method."

2. Copper and lead may also be determined simultaneously by the electrolytic method. See "Analysis of Manganese Bronze."

3. For amounts of lead less than 0.2% proceed as in "Determination of Lead as Sulfate, Analysis of Manganese Bronze."

DETERMINATION OF IRON

Solutions Required. ***Yellow Ammonium Sulfide and Dilute Yellow Ammonium Sulfide for Washing.***—See " Determination of Tin."

Other Solutions.—See " Determination of Iron, Analysis of Manganese Bronze."

Method.—Proceed exactly as in " Determination of Copper " up to the point where the tin has been separated as H_2SnO_3.

Retain both the filtrate and the precipitate. Transfer the papers with the precipitate to a 150-ml. beaker, and cover them with 40 to 50 ml. of yellow ammonium sulfide. Warm about 15 minutes, or until the meta-stannic acid is dissolved. Filter and wash thoroughly with hot, dilute yellow ammonium sulfide.

Dissolve the small black residue on the filter with hot dilute HCl, receiving the solution in a small beaker. Add 5 ml. of HNO_3 (sp.gr. 1.42) and boil to oxidize sulfur and iron. Add this small solution to the original filtrate from the meta-stannic acid. Add about 5 g. of NH_4Cl, then NH_4OH (sp.gr. 0.90) and proceed as in the " Determination of Iron, Analysis of Manganese Bronze."

DETERMINATION OF NICKEL BY THE DIMETHYLGLYOXIME METHOD

Solutions Required. ***Dimethylglyoxime Solution.***—Dissolve 5 g. of dimethylglyoxime in 500 ml. of grain alcohol, and filter before using.

Sodium Potassium Tartrate Solution.—Dissolve 200 g. of the salt in 1 liter of distilled water.

Dilute Ammonia for Washing.—Solution containing 10 ml. of NH_4OH (sp.gr. 0.90) per liter of water.

Method.—In a 150-ml. electrolytic beaker, dissolve a 1 g. sample of the bronze in 10 ml. of HNO_3 (sp.gr. 1.42) and remove tin and copper exactly as described in the " Determination of Copper by the Electrolytic Method." Evaporate the solution to about 100 ml., filter, add about 1 g. of NH_4Cl, then 10 ml. of sodium potassium tartrate solution, and nearly neutralize with NH_4OH (sp.gr. 0.90). Heat nearly to boiling, add 5 ml. of dimethylglyoxime solution for each 0.01 g. or fraction of nickel present and then NH_4OH in slight excess. Let stand at least 30 minutes on the steam bath, filter and wash with dilute ammonia solution. For accurate work, the precipitate should be dissolved in hot HCl (1 : 1) and reprecipitated as before. Filter on a weighed Gooch crucible, wash with dilute ammonia solution, and then with hot water; dry at 110 to 120° C. for about two hours and weigh as the glyoxime salt which contains 20.32% of nickel. If it is preferred, instead of by weighing the glyoxime salt, the nickel can be determined electrolytically as follows: Dissolve the red precipitate of nickel glyoxime in hot HCl (1 : 1), add 10 ml. of H_2SO_4 (1 : 1) and evaporate to strong fumes. Dilute, neutralize with NH_4OH (sp.gr.

0.90), and add 20 ml. in excess. The final volume should be about 150 ml. Electrolyze with a current of 0.3 ampere per solution. Test the solution for completion of deposition with fresh H_2S water as is done in the "Determination of Copper by the Electrolytic Method." Remove the cathode, wash with water and dry with alcohol as in the "Determination of Copper by the Electrolytic Method." Weigh the deposit as metallic nickel.

DETERMINATION OF ZINC

After the copper has been completely deposited by electrolysis, quickly remove the cathode and wash it thoroughly with distilled water, catching the washings in the beaker containing the electrolyte. Heat the solution and saturate with H_2S gas. Filter off any precipitate, and boil the solution to expel H_2S. Make the solution barely alkaline with NH_4OH, and add 25 ml. of 85% formic acid. Dilute the solution with distilled water to 300 ml., heat to boiling, and saturate with H_2S gas. Filter, wash with hot water and dissolve the precipitate with hot HCl (1 : 1) and transfer the solution to a weighed platinum or porcelain dish or crucible. Add a few drops of H_2SO_4 (sp.gr. 1.84) and evaporate the solution until copious fumes escape. If the solution is not clear and colorless, cool, add a few milliliters of HNO_3 (sp.gr. 1.42) and again evaporate the solution until fumes of H_2SO_4 come off freely. Repeat the treatment with HNO_3, if necessary, until the organic matter is destroyed, and the solution is colorless. Remove the excess of H_2SO_4 by heating the dish cautiously, and finally heat to dull redness. Weigh as $ZnSO_4$ and calculate to Zn.

DETERMINATION OF PHOSPHORUS BY THE ALKALIMETRIC METHOD

Solutions Required. *Nitric Acid for Dissolving.*—Mix 1000 ml. of HNO_3 (sp.gr. 1.42) and 1200 ml. of distilled water.

Nitric Acid for Washing.—Mix 20 ml. of HNO_3 (sp.gr. 1.42) and 1000 ml. of distilled water.

Ammonium Molybdate Solution No. 1.—Place in a beaker 100 g. of 85% molybdic acid, mix it thoroughly with 240 ml. of distilled water, add 140 ml. of NH_4OH (sp.gr. 0.90), filter and add 60 ml. of HNO_3 (sp.gr. 1.42).

Ammonium Molybdate Solution No. 2.—Mix 400 ml. of HNO_3 (sp.gr. 1.42) and 960 ml. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.1 g. of ammonium phosphate dissolved in 10 ml. of distilled water and let stand at least 24 hours before using.

Potassium Nitrate, 1% Solution.—Dissolve 10 g. of potassium nitrate in 1000 ml. of distilled water.

Phenolphthalein Indicator.—Dissolve 0.2 g. in 50 ml. of 95% ethyl alcohol and 50 ml. of distilled water.

Standard Sodium Hydroxide.—Dissolve 3.3 g. of purified NaOH in 1000 ml. of distilled water, add a slight excess of 1% solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of known phosphorus content as determined by the molybdate-magnesia method.

so that 1 ml. will be equivalent to 0.01% of phosphorus on the basis of a 1 g. sample (see Notes). Protect the solution from carbon dioxide with a soda-lime tube.

Ferric Chloride.—Dissolve 100 g. of ferric chloride (phosphorus free) in 100 ml. of distilled water.

Standard Nitric Acid.—Mix 5 ml. of HNO_3 (sp.gr. 1.42) and 1000 ml. of distilled water. Titrate the solution against standardized NaOH, using phenolphthalein as indicator, and make it equivalent to the sodium hydroxide by adding distilled water.

Method.—In a 400-ml. beaker, dissolve a 1 g. sample in 10 ml. of HNO_3 (sp.gr. 1.42) and heat until brown fumes are driven off; then add 15 ml. of HCl (sp.gr. 1.18) and evaporate to dryness. Add 10 ml. of HCl (sp.gr. 1.18) and again evaporate to dryness, but do not bake.

Add 15 ml. of HCl (sp.gr. 1.18) and heat to solution; dilute with 50 ml. of distilled water and bring to a boil. Take off the hot plate and wash down the cover glass and sides of the beaker, add 20-mesh c.p. zinc, 2 or 3 g. at a time until the solution becomes colorless, that is, until all the copper, tin and lead are precipitated. Filter, receiving the filtrate in a 400-ml. beaker, and wash well with hot water.

Add 3 ml. of the ferric chloride solution to this filtrate and make faintly ammoniacal; bring to a boil, let settle and filter. Dissolve this precipitate in hot dilute HCl and again make ammoniacal; heat to boiling, let settle and filter, washing well with hot water.

Dissolve this precipitate in as small a quantity of hot dilute HNO_3 as possible, receiving the solution in a 300-ml. Erlenmeyer flask; wash filter free of iron with hot dilute HNO_3 and hot distilled water. Evaporate to about 15 ml., cool, make ammoniacal, then neutralize with HNO_3 (sp.gr. 1.42) and add 5 ml. in excess. Cool to 80° C., and add 60 ml. of the ammonium molybdate solution. Let stand one minute, then shake three minutes and let settle. Filter on an 11 cm. filter (using a small quantity of paper pulp on the filter) and wash free of iron with 2% nitric acid wash, then free of acid with the 1% potassium nitrate solution.

Place the paper in the thoroughly washed acid-free flask in which the original precipitation was made, add 25 ml. of distilled water and an excess of the standard sodium hydroxide solution. By using a long glass rod, the paper can be pulped and the yellow precipitate dissolved in a very few seconds. Wash off the rod and the sides of the flask and add a few drops of the phenolphthalein solution and titrate the excess of standard NaOH with the standard HNO_3. The strength of the standard NaOH and the standard HNO_3 in terms of phosphorus can be determined by using a standard steel or preferably a standard phosphor bronze in which the phosphorus has been determined by the molybdate-magnesia method.

Accuracy.—Duplicate determinations should check within 0.01% of phosphorus.

Notes.—1. The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

2. All distilled water used in titration should be freed from carbon dioxide by boiling or otherwise.

3. Bureau of Standards Steel No. 19 (a) or a bronze of known phosphorus content are recommended as suitable materials for standardization of the sodium hydroxide solution.

4. (Gravimetric method, optional.) It is considered by some that more accurate results can be obtained by a gravimetric determination of phosphorus as $Mg_2P_2O_7$. This can be carried out by dissolving the yellow molybdate precipitate in 20 ml. of NH_4OH (1 : 1) to which has been added 2 g. of citric acid, precipitating with magnesia mixture, and proceeding as usual, finally weighing as $Mg_2P_2O_7$.

DETERMINATION OF PHOSPHORUS BY THE FERRIC-ALUM METHOD [9] (Optional)

Solutions Required. *Ferric Chloride.*—Dissolve 100 g. of ferric chloride (phosphorus free) in 100 ml. of distilled water.

Dilute Ammonia.—Mix 100 ml. of NH_4OH (sp.gr. 0.90), and 900 ml. of distilled water.

Dilute Hydrochloric Acid.—Mix 500 ml. of HCl (sp.gr. 1.18), and 500 ml. of distilled water.

Dilute Sulfuric Acid for Dissolving.—Mix 200 ml. of H_2SO_4 (sp.gr. 1.84), and 800 ml. of distilled water.

Dilute Sulfuric Acid for Reductor.—Mix 50 ml. of H_2SO_4 (sp.gr. 1.84), and 1000 ml. of distilled water. This solution is used boiling hot.

Ammonium Molybdate.—Solution No. 1. Place in a beaker 100 g. of 85% molybdic acid, mix it thoroughly with 240 ml. of distilled water, add 140 ml. of NH_4OH (sp.gr. 0.90), filter and add 60 ml. of HNO_3 (sp.gr. 1.42).

Solution No. 2. Mix 400 ml. of HNO_3 (sp.gr. 1.42), and 960 ml. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly, then add 0.1 g. of ammonium phosphate dissolved in 10 ml. of distilled water, and let stand at least 24 hours before using.

Acid Ammonium Sulfate.—Mix 25 ml. of H_2SO_4 (sp.gr. 1.84), and 1000 ml. of distilled water, and then add 15 ml. of NH_4OH (sp.gr. 0.90).

Ferric Alum.—Dissolve 200 g. of ferric ammonium sulfate crystals in 1950 ml. of distilled water. Add 50 ml. of H_2SO_4 (sp.gr. 1.84), and 80 ml. of phosphoric acid, 85%.

Potassium Permanganate.—Dissolve from 3.0 to 3.2 g. of $KMnO_4$ in 1000 ml. of distilled water. Allow the solution to stand for about one week, and then filter it through an asbestos filter. Standardize by using about 0.200 g. portions of pure sodium oxalate.

Method.—In a 400-ml. casserole dissolve 1 g. of sample in 10 ml. of HNO_3 (sp.gr. 1.42). Add 20 ml. of HCl (sp.gr. 1.18), and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again, add 3 ml. of ferric chloride solution, and dilute to about 200 ml. with distilled water. Add NH_4OH (sp.gr. 0.90) until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl, dilute the solution to about 200 ml., add NH_4OH (sp.gr. 0.90) until the precipitate which forms at first dissolves rather slowly, and saturate

[9] A. S. T. M. Methods of Chemical Analysis of Metals, p. 154, December, 1936.

with H_2S gas. Filter off and reject the precipitate. Boil the filtrate to expel H_2S, and add HNO_3 (sp.gr. 1.42) until the iron is oxidized. Add NH_4OH (sp.gr. 0.90) until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute H_2SO_4, receiving the solution in a 350-ml. Erlenmeyer flask. Add NH_4OH (sp.gr. 0.90) until the iron is entirely precipitated, and then add HNO_3 (sp.gr. 1.42) cautiously until the solution just becomes clear. Bring the solution to a temperature of about 80° C., and add 40 ml. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, filter on a 9 cm. paper, and wash very thoroughly (about 25 times) with acid ammonium sulfate. Dissolve the precipitate on the paper using 50 ml. of dilute ammonia. Add sufficient H_2SO_4 to adjust the acidity to 2.5% by volume and immediately pass the solution through a Jones reductor, which has the reductor tube prolonged and reaching nearly to the bottom of the flask, dipping into 50 ml. of ferric-alum solution. Wash through the reductor with 150 ml. of the H_2SO_4 for reductor and follow with an additional 100 ml. of distilled water. Titrate with standard $KMnO_4$.

By this method the molybdenum which in passing through the reductor has been reduced entirely to the form corresponding to the oxide Mo_2O_3 is partially oxidized by the ferric alum, an equivalent amount of iron being reduced to the ferrous condition. The resultant solution is not rapidly oxidized through contact with air during the titration, and the calculations can therefore be made on the $Mo_2O_3 - 2MoO_3$ basis.

Accuracy.—Duplicate determinations should check within 0.01% of phosphorus.

Notes.—The ammonium-molybdate solution should be kept in a cool place and should always be filtered before using.

A blank determination should be made on corresponding amounts of acid and water, passing through the reductor into the usual amount of ferric-alum solution in the flask.

A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the reductor.

For a description of the Jones reductor consult, "Determination of Iron, Analysis of Manganese Bronze."

DETERMINATION OF ANTIMONY BY THE VOLUMETRIC METHOD

Solutions Required. ***Potassium Permanganate.***—Dissolve 0.3 g. of potassium permanganate in 1000 ml. of distilled water. Standardize by dissolving 25 mg. of pure antimony in 15 ml. of boiling sulfuric acid and proceed according to the method from this point.

Method.—In a 250-ml. beaker, dissolve 5 g. of bronze in 25 ml. of HNO_3 (sp.gr. 1.42). When the action has ceased, boil until the oxides of nitrogen are expelled, add 125 ml. of boiling water and allow to stand and settle for one hour or longer, keeping the temperature just below the boiling point. Filter on double 9 cm. closely woven papers, keeping the solution hot. Wash with boiling water. Discard the filtrate.

Transfer the papers containing the tin and antimony to a 350-ml. Erlenmeyer flask and add 25 ml. of HNO_3 (sp.gr. 1.42), 5 g. of ammonium persulfate, and 15 ml. of H_2SO_4 (sp.gr. 1.84). Boil to strong fumes of SO_3. If the solution is brown, cool and add 5 ml. of HNO_3 (sp.gr. 1.42) and a little more (1 g. or less) persulfate, if necessary, and boil again to strong fumes of SO_3. When the solution is colorless, cool, add 20 ml. of distilled water 20 ml. of HCl (sp.gr. 1.18) and 1 g. of sodium sulfite. Boil gently for 10 minutes to expel SO_2 completely. Dilute with 200 ml. of distilled water and cool to 10 to 12° C. in ice or under running water.

Titrate with standard permanganate solution until the appearance of a decided pink color.

NOTES.—1. In alloys containing a large excess of tin, the antimony is precipitated quantitatively with the meta-stannic acid.

2. Ammonium persulfate and nitric acid are used to destroy the filter paper, and subsequent boiling with sulfuric acid effects the solution of the tin and antimony. A mixture of fuming nitric and sulfuric acids might be used to accomplish the same results, but the persulfate mixture is much more efficient.

3. If the solution becomes cool during the first filtration, some of the meta-stannic acid may dissolve.

4. If arsenic is present, correction should be made for it.

DETERMINATION OF SULFUR

Method.—Weigh out four 5 g. samples of bronze into 250-ml. beakers. Dissolve each in 25 ml. of HNO_3 (sp.gr. 1.42) and boil until the disappearance of red fumes. Add 125 ml. of boiling water and allow to settle for one hour or longer, keeping the temperature just below the boiling point. Filter on double 12.5 cm. closely woven papers, keeping the solution hot. Wash with boiling water. Discard the meta-stannic acid precipitates, combine the four filtrates in a tall 700-ml. beaker and add 0.5 g. of sodium carbonate, and evaporate the solution until syrupy. Cool somewhat, then dilute to the lip with warm water. There should be present a layer about 6 mm. in thickness, composed of basic salts of copper. Electrolyze, using large stationary electrodes, at a current of 4 amperes, or using the Frary solenoid at a current of about 10 amperes. The lead must be removed at the anode as the copper is taken out at the cathode. When copper and lead are out, evaporate the electrolyte to small volume, cover the beaker, add 75 ml. of HCl (sp.gr. 1.18) and boil down to small volume. Add 75 ml. more HCl and evaporate to dryness to dehydrate any silica present. Moisten with about 0.5 ml. of HCl and take up with 20 ml. of hot water. Filter into a small beaker. Heat the filtrate to boiling and add 10 ml. of 5% $BaCl_2$ solution, drop by drop, with stirring. Allow to settle at least five hours, filter on a small ashless paper, and wash with hot water. Ignite cautiously in a small porcelain or platinum crucible, and then heat to a bright redness for 20 minutes. Cool and weigh the $BaSO_4$ and calculate to sulfur.

NOTES.—1. Throughout the entire analysis, the utmost precautions must be taken to prevent contamination by sulfur in any form, H_2SO_4 fumes, H_2S and SO_2 gases especially. All heating with gas burners must be avoided. Run a blank with each analysis, adding the reagents and subjecting it to the same operations as the beakers containing the drillings. Subtract the amount of $BaSO_4$ found in the blank from that in the deter-

minations. If this blank amounts to 0.002 g., it is a sign of poor work or impure reagents and the analysis should be repeated. Wash out all beakers, funnels, etc., with distilled water before using.

2. It is necessary to keep the solution containing the meta-stannic acid hot during filtration. If the solution becomes cool, some of the meta-stannic acid may dissolve.

DETERMINATION OF ARSENIC

Solutions Required. *Ammonium Carbonate.*—Dissolve 150 g. of ammonium carbonate in one liter of distilled water.

Method.—Dissolve the sample (5.00 to 10.00 g.) in a 100-ml. beaker in 10 ml. of HNO_3 (sp.gr. 1.42) and 30 ml. of HCl (sp.gr. 1.18). When solution is complete, cool, add 35 ml. of H_2SO_4 (sp.gr. 1.84), evaporate to the appearance of copious fumes of H_2SO_4, and continue the fuming for from ten to fifteen minutes. Cool, take up in HCl (sp.gr. 1.18), transfer to an 800-ml. flask having a two-hole stopper with separatory funnel and outlet tube connecting with a vertical condenser outside. (The part of the outlet tube within the distilling flask should have a steam outlet hole about 1 cm. from the open end.) Rinse the beaker with HCl (sp.gr. 1.18) and dilute the solution with the acid to make a total volume of 350 to 450 ml. Add 10 g. of cuprous chloride (Cu_2Cl_2), connect the flask with the condenser, and gradually raise the contents of the flask to boiling. Catch the distillate in a tall 400-ml. beaker containing 100 ml. of cold water. The end of the condenser should extend several millimeters into the water in the beaker and the beaker should be surrounded with ice water in order to avoid any possible volatilization of arsenious chloride. After about 100 ml. of distillate has passed over, remove the flame from the distilling flask, pour 3 to 5 ml. of hypophosphorus acid through the separatory funnel into the distilling flask, and redistill as before, catching the distillate in the same beaker. The volume of the second distillate should be 50 to 100 ml. Pass a rapid current of H_2S through the distillate for one hour, allow to settle, and filter on a weighed Gooch crucible. Wash twice with HCl (1 : 1), four times with cold water, three times with alcohol, and four times with CS_2. Dry at 110° C. for 10 minutes, and weigh after cooling. Dissolve the As_2S_3 with $(NH_4)_2CO_3$ solution, wash thoroughly with water, dry for 30 minutes at 110° C. and reweigh after cooling. The difference in weights multiplied by 0.609 gives the weight of arsenic.

Note.—Blank determinations should be made on the reagents carried along as in the method and the proper corrections made.

THE DETERMINATION OF CADMIUM IN BRASS

General Considerations.—From the results of a series of experiments on known synthetic mixtures, it was found that the following method is satisfactory even in the presence of moderate amounts of arsenic, lead, bismuth, tin and antimony.

Method.—Prepare a sufficient amount of sawdust or drillings from the brass to be tested to furnish at least a twenty-gram sample. For the assay weigh ten grams of this sample into a 500-ml. Erlenmeyer flask and dissolve in concentrated nitric acid. Add 50 ml. concentrated H_2SO_4 and fume strongly. Cool

and dilute to 200 ml. with water, boil for a few minutes and allow to cool. After two or three hours filter off any insoluble matter, collecting the filtrate in a tall 600-ml. beaker. Discard the residue on the paper and dilute the filtrate to 400 ml. Heat to boiling and pass a rapid stream of H_2S through this hot solution for thirty minutes. (It is well to thoroughly mix the copper sulfide with the solution by means of rubber-tipped rod so as to keep the precipitate from being forced out of the solution by the gas.)

At the end of the half hour filter off the precipitated sulfides on an 18½ cm. paper, receiving the filtrate in a tall 600-ml. beaker. Wash the sulfides once with hot water. If proper precipitation has been made, this filtration will be rapid and easy to make and the filtrate will have no blue color. Return the precipitated sulfides with the filter paper to the beaker in which precipitation was made and add 400 ml. of 10% H_2SO_4. Boil vigorously for a half hour and filter hot on a 19½ cm. paper. Wash the residue thoroughly with boiling water. Discard the residue on the paper. All of the cadmium is now present in these two solutions.

Cool and pass a rapid stream of H_2S through the solution for ten minutes. Add ammonia slowly to each solution until zinc sulfide begins to precipitate. When this is certain, continue the passage of the gas for five minutes more and then filter off the precipitates separately on 12½ cm. paper. Discard the filtrates. Combine the two papers containing mixed sulfides and boil with 100 ml. of 10% H_2SO_4 for ten minutes, stirring frequently. Filter and wash. Cool and dilute to 300 ml. Pass in H_2S and add ammonia drop by drop until cadmium is entirely precipitated. Pass gas for about twenty minutes. Filter the precipitate on an 11 cm. close texture paper. Return the paper to the beaker and boil with 50 ml. of 10% H_2SO_4. Filter and wash. Dilute to 300 ml. and pass in H_2S for twenty minutes. A drop or two of ammonia will be sufficient to start the precipitation of cadmium.

Filter the cadmium sulfides on a weighed Gooch crucible. Wash twice with cold water. Dry at 110° C. for two hours and reweigh.

$$\text{Weight CdS} \times 0.778 = \text{Weight cadmium.}$$

The final cadmium sulfide precipitate will have a characteristic bright, yellow color and will be entirely free of other sulfides if the foregoing directions be carefully followed.

As a special precaution when arsenic or tin are suspected in the brass the final sulfide may be washed out of the crucible after weighing and treated with yellow ammonium sulfide. (The addition of NH_4Cl will tend to prevent cadmium sulfide being carried into the ammonium sulfide solution as a colloid.) Filter and wash the residue and dissolve the cadmium sulfide in 10% H_2SO_4, reprecipitate and weigh again.

ANALYSIS OF COPPER, NICKEL, ZINC ALLOYS

ANALYSIS OF GERMAN SILVER
(ALLOY OF COPPER, NICKEL AND ZINC)

DETERMINATION OF TIN, COPPER AND LEAD

Proceed exactly as in the determination of these elements under " Analysis of Manganese Bronze."

DETERMINATION OF IRON

Solutions Required. ***Stannous Chloride.***—Dissolve 450 g. of the salt in 380 ml. of concentrated HCl (sp.gr. 1.18) to which some water has been added and dilute to 2 liters.

Mercuric Chloride.—Make a saturated solution of the salt in hot water, allow to cool to room temperature and filter.

Manganese Sulfate.—Dissolve 160 g. of the salt in water and dilute to 1750 ml. To this add 330 ml. of phosphoric acid (sp.gr. 1.70) and 320 ml. of sulfuric acid (sp.gr. 1.84). This solution is to obviate the deterious action of hydrochloric acid upon the standard potassium permanganate. The phosphoric acid allows the formation of iron phosphate, which, being nearly colorless, renders the end reaction more distinct.

Potassium Permanganate.—Make a solution containing 0.3163 g. of salt per liter. This is approximately N/100.

Standardization of above Permanganate Solution.—Take measured quantities of a carefully standardized ferric chloride solution, containing 5 g. of metallic iron and 100 ml. concentrated hydrochloric acid to a liter in No. 1 beakers. About 5 ml. of this solution should prove adequate. Add from a burette stannous chloride solution until the iron is almost reduced, told by the color change. Then heat to boiling and reduce iron completely with $SnCl_2$, using a slight excess of the reagent. Add 5 ml. of $HgCl_2$ solution to oxidize excess of $SnCl_2$. Pour solution into a 600-ml. beaker containing 6—8 ml. of the $MnSO_4$ solution in 400 ml. of water. Titrate with $KMnO_4$ immediately until a faint pink is obtained. Calculate potassium permanganate in terms of metallic iron.

Treatment of Sample.—Weigh out a 5 g. sample of drillings from which all steel chips have been removed by a magnet and transfer to a 250-ml. beaker. Dissolve in as little nitric acid (sp.gr. 1.42) as possible (25 ml. should be sufficient), heat until all nitric oxide fumes have been driven off and then dilute to 100 ml. with distilled water. Add 3 to 4 g. of ammonium chloride crystals, heat to boiling, and add a slight excess of ammonia to precipitate all the iron as hydroxide.

A small amount of zinc is usually precipitated at this point as hydroxide and also, if manganese is present in the alloy, it will come down as manganese hydroxide.

After the precipitate has settled down, filter through filter paper and wash with ammonium hydroxide 1 : 4 until all soluble salts are removed (or until

the blue copper color has been washed from the filter paper). Treat the precipitate on the filter paper with a little hot HCl (1 : 1), catching the resulting solution in original beaker. Wash the filter paper alternately with hot water and HCl (1 : 1) until the iron has been completely removed. Dilute the hydrochloric acid solution in the beaker to about 75 ml. and add 3–4 g. of ammonium chloride. Heat to boiling and reprecipitate the iron with a slight excess of ammonium hydroxide. Filter and wash as before. (A double precipitation is usually sufficient to remove zinc, etc.) Dissolve the precipitate in a small amount of hydrochloric acid (1 : 1). Add stannous chloride to reduce the iron—2 or 3 drops are usually sufficient.

Heat almost to boiling and add 1 or 2 drops more of stannous chloride to be sure an excess is present. Run in an excess of mercuric chloride solution (about 5 ml.) to oxidize the stannous chloride.

Pour into a 600-ml. beaker containing 6–8 ml. of the manganese sulfate solution in 400 ml. of water.

Titrate with standard potassium permanganate solution until a slight pink opalescence is obtained.

DETERMINATION OF MANGANESE

Proceed exactly as in " Determination of Manganese by the Persulfate Method " or " Determination of Manganese by the Bismuthate Method," under " Analysis of Manganese Bronze."

DETERMINATION OF NICKEL

Solutions Required. ***Standard Solution of Potassium Cyanide.***—Dissolve 26 g. of pure potassium cyanide in 1000 ml. of distilled water and add 1.25 g. of silver nitrate. This solution is standardized against a solution of known metal content.

Potassium Iodide.—Dissolve 100 g. of c.p. potassium iodide crystals in 1000 ml. of distilled water.

Sodium Pyrophosphate.—Make a saturated solution of c.p. sodium pyrophosphate crystals in distilled water.

Method.—See the " Determination of Copper, Lead and Tin."

Transfer the electrolyte and washings from the electrolytic determination of copper to a 400-ml. beaker. Add 3 to 4 g. of ammonium chloride and then 50 to 75 ml. of a saturated solution of sodium pyrophosphate, depending upon the amount of zinc present. Neutralize with ammonium hydroxide (sp.gr. 0.90) and then add enough to make the solution only slightly but yet distinctly alkaline. A large excess of ammonia will hinder or entirely prevent the reaction. Cool, and do not let the temperature get much above 20° C. or the result will be irregular. Add 2 ml. of a 10% solution of potassium iodide and titrate with a standard solution of potassium cyanide containing silver nitrate until the white cloud caused by the formation of silver iodide has entirely disappeared and one drop of the cyanide causes a clear solution. This is the end point which is very sharp and distinct.

NOTES.—The method of estimating nickel by means of adding potassium cyanide to an ammoniacal solution of nickel containing silver iodide in suspension so that the solution remained turbid until the nickel was all converted into the double cyanide of nickel and potassium, after which a single drop of the cyanide in excess cleared up the solution, was originally proposed by T. Moore and modified by W. B. Price for use in the determination of nickel in German silver, etc.

The following elements interfere with the method: Manganese, zinc, iron, aluminum and especially copper, which, owing to its forming cyanides, would render the method valueless. Cobalt, if present, will be estimated as nickel. The iron, aluminum and zinc may be kept in solution so that they do not interfere by the use of organic acids such as tartaric or citric or with sodium pyrophosphate.

DETERMINATION OF ZINC

Zinc is usually taken by difference.

In case an actual determination is desired proceed exactly as in " Determination of Zinc, Analysis of Bronze Bearing Metals."

ANALYSIS OF BISMUTH BRONZE

(ALLOY OF COPPER, TIN, BISMUTH, NICKEL AND ZINC)

General Considerations.—Bismuth will interfere with the electrolytic determination of copper and must be removed before this determination can be made.

DETERMINATION OF TIN

Proceed exactly as in " Determination of Tin, Analysis of Bronze Bearing Metal."

DETERMINATION OF LEAD

To the filtrate from the H_2SnO_3 separation, add 8 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate until copious fumes of H_2SO_4 are evolved. Cool, add 30 ml. of distilled water and boil until all bismuth sulfate is dissolved. Cool, filter on a weighed Gooch crucible and wash with cold dilute H_2SO_4 (10%). Filter as soon as possible, otherwise some basic bismuth sulfate will separate out. Set the Gooch crucible inside a porcelain crucible, dry, ignite for 5 minutes at the full heat of a Tirrill burner, cool and weigh as $PbSO_4$ which contains 68.33% of lead.

NOTE.—A small amount of lead still remains in the solution to be recovered later. (See Note: "Determination of Bismuth.")

DETERMINATION OF COPPER

To the filtrate from the $PbSO_4$ separation add 0.1 g. of iron wire dissolved in 10 ml. of HNO_3 (sp.gr. 1.42) and then add NH_4OH (sp.gr. 0.9) in sufficient excess to hold the copper in solution. Now add 10 ml. of a saturated solution of ammonium carbonate, bring to boiling, filter and wash with hot water containing a small amount of $(NH_4)_2CO_3$. Reserve the filtrate. Wash the precipitate back into the original beaker and dissolve any remaining precipitate on the paper with 20 ml. of hot HNO_3 (1 : 2) catching the resulting solution in the original beaker. Wash several times with hot water. Warm until the precipitate is completely dissolved and make a second separation of iron and bismuth with ammonium hydroxide and ammonium carbonate. Again dissolve the precipitate with nitric acid and make a third separation. Hold the residue.

Combine the three filtrates and washings from the separation of iron and bismuth, which should not exceed 400 ml., make just acid with H_2SO_4 (1 : 1), add 10 ml. in excess, and evaporate down to a volume of 100 ml. Cool, add 1.5 ml. of HNO_3 (sp.gr. 1.42) and electrolyze for copper. (See " Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze.")

DETERMINATION OF BISMUTH

Treat the precipitate containing the bismuth and iron on the paper with a little hot HCl (1 : 1) catching the resulting solution in a clean beaker. Wash the paper alternately with hot water and hot dilute HCl (1 : 1) until the bismuth has been completely removed. Neutralize the free acid with NH_4OH (sp.gr. 0.9), make slightly acid with HCl and pass H_2S. Filter and wash with H_2S water. (Discard the filtrate unless it is desired to run zinc or nickel on this portion.)

Wash the precipitate of bismuth sulfide back into the beaker and pour through the filter paper 30 ml. of hot HNO_3 (1 : 2) catching the solution in the same beaker. Wash a few times with hot water. Heat the solution until the precipitate is completely dissolved. Filter through the same filter paper and wash with hot dilute HNO_3 (1 : 50). If a black insoluble residue still remains, transfer the residue to a small porcelain crucible, dry, ignite over a low flame, cool, dissolve in 1 ml. of HNO_3 (sp.gr. 1.42) and combine with the main filtrate. Boil the combined solutions down to a volume of 60 ml. and allow to stand and settle for one hour keeping the temperature just below the boiling point. If a precipitate of H_2SnO_3 forms, filter, wash, dry, ignite and weigh as SnO_2. Add the weight found to that already obtained (see " Determination of Tin.").

Evaporate the filtrate to a volume of about 50 ml., make just neutral with NH_4OH (1 : 3) and then add 5 ml. of HCl (1 : 9) in excess. If a precipitate of BiOCl forms, cautiously heat until it goes into solution. Dilute to a volume of 400 ml. with boiling hot water and allow to stand in a warm place several hours. Filter on a weighed porcelain Gooch crucible and wash with hot water. Finally wash once with 95% alcohol but transfer the filtrate to a clean beaker before doing so. Dry at 110° C. for 30 minutes, cool and weigh as BiOCl. Multiply by 0.8025 for bismuth.

NOTE.—The filtrate from the BiOCl separation contains a small amount of lead that did not precipitate out as $PbSO_4$ (see "Determination of Lead"). This may be recovered in the following manner: make the solution just alkaline with ammonium hydroxide, pass H_2S, filter and wash. Dissolve the precipitate from the filter paper with 15 ml. of hot HNO_3 (1 : 2) and wash with hot water. Add 12 ml. of HNO_3 (sp.gr. 1.42), dilute to a volume of 150 ml. with distilled water and electrolyze for lead (see "Determination of Lead by the Electrolytic Method, Analysis of Manganese Bronze"). Add the weight of lead found to that already obtained.

DETERMINATION OF NICKEL

Method.—Remove the tin and lead as in "Determination of Tin" and "Determination of Lead." Remove the copper by electrolysis (see "Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze"). Continue as in "Determination of Nickel, Analysis of German Silver."

NOTE.—1. If the amount of lead is small, the copper and lead may be removed at the same time by electrolysis (see "Determination of Copper and Lead Simultaneously by the Electrolytic Method, Analysis of Manganese Bronze"). It is not necessary to evaporate to dryness.

2. The presence of a moderate amount of bismuth will not prevent the electrolytic precipitation of copper. The deposit, however, will be black and possibly spongy, and may slough off in washing, in which case, filter and wash and combine washings and main filtrate. If the spongy material has dropped off into the electrolyte it will dissolve. In such a case filter both electrolyte and washings through the same paper, wash, combine filtrate and washings, pass H_2S, filter and wash, boil to expel H_2S, oxidize the iron with HNO_3 (sp.gr. 1.42) and proceed as directed above.

DETERMINATION OF ZINC

Method.—Remove the tin, lead and copper as directed under "Determination of Nickel." Continue as in "Determination of Zinc, Analysis of Bronze Bearing Metal."

DETERMINATION OF IRON

Method.—Proceed exactly as in "Determination of Iron, Analysis of Bronze Bearing Metal," up to the point where the H_2SnO_3 has been separated and any iron present in the H_2SnO_3 has been recovered and combined with the main filtrate. Add 5 g. of ammonium chloride crystals, and a slight excess of NH_4OH (sp.gr. 0.9). Boil, allow to settle, filter on a loosely woven filter paper and wash with dilute ammonium hydroxide and with hot water. Treat the precipitate on the paper with a little hot HCl (1 : 1) catching the resulting solution in original beaker. Wash the filter paper alternately with hot water and HCl (1 : 1) until the iron has been completely removed. Neutralize the solution with NH_4OH (sp.gr. 0.9), make acid with 5 ml. of HCl (sp.gr. 1.18) in excess, dilute to a volume of 100 ml., warm and pass H_2S. Filter and wash with hot water. Boil the filtrate to expel H_2S, add a few ml. of HNO_3 (sp.gr. 1.42) to oxidize the iron, dilute to a volume of 75 ml., add 3 to 4 g. of ammonium chloride crystals, and a slight excess of NH_4OH (sp.gr. 0.9) and continue as in "Determination of Iron, Analysis of German Silver."

DETERMINATION OF ALUMINUM

Proceed exactly as in " Determination of Aluminum, Analysis of Manganese Bronze."

DETERMINATION OF MANGANESE

Proceed exactly as in " Determination of Manganese, Analysis of Manganese Bronze."

COPPER NICKEL ALLOYS

ANALYSIS OF MONEL METAL[10]

(ALLOY OF Ni, Cu, AND IRON)

Determination of Copper and Nickel

Electrodes.—See " Analysis of Manganese Bronze."

Method.—Dissolve one gram of drillings in 15 ml. of nitric acid (1 : 1) in a 200-ml. covered beaker. Add 30 ml. of sulfuric acid (1 : 1), and evaporate until fumes of sulfuric acid are given off. Dilute with 125 ml. of water, heat on hot plate until sulfates are dissolved. Add 1.5 ml. of nitric acid, cool and plate out copper over night with a current of 0.3 amp. After copper is all plated out pour the solution and water used in washing off cathode, into a 500-ml. beaker. The cathode is dipped in alcohol and heated over an alcohol lamp and when cool, weighed. The increased weight is equal to copper. The solution in the beaker is covered, made alkaline with ammonia, and 75 ml. added in excess. To 30 ml. of cold water add about 2 grams of sodium peroxide. Add this solution to the alkaline nickel solution and let stand on the steam bath for one-half hour. Repeat the addition of sodium peroxide solution, then cool the alkaline nickel solution, and when cold plate nickel over night with a current of 0.5 amp. Wash the cathode with water and alcohol. Heat over an alcohol lamp and when cool weigh as nickel and cobalt. The nickel and cobalt contain a small amount of manganese, so dissolve the nickel and cobalt in nitric acid and determine the manganese by the bismuthate method. This is deducted, the result being nickel and cobalt.

Monel Metal contains a small amount of cobalt. If nickel, exclusive of cobalt, is desired dissolve the deposit with hot nitric acid, transfer to a 250 ml. graduated flask, dilute to the mark with cold water, mix and draw off exactly 50 ml. Proceed as described in " Determination of Nickel, Analysis of Bronze Bearing Metals."

[10] See "Tentative Methods of Chemical Analysis of Nickel," A. S. T. M. Methods of Chemical Analysis of Metals, p. 226, December, 1936.

NOTE.—In very accurate determinations the solution, after plating out the nickel and cobalt, is evaporated down, made acid with sulfuric acid, make alkaline with ammonia, sodium peroxide added and replated, same as above.

DETERMINATION OF IRON

Solutions Required. ***Cuprous Chloride Solution.***—Place into a 2-liter heavy glass bottle, 400 g. of NaCl, 100 ml. of HCl (sp.gr. (1.18) and 20 g. of Cu_2Cl_2. Add 2 liters of warm water; shake well; place into the solution a few copper rods and let stand over night in a cool place. After shaking, the solution is ready for use. One milliliter of Cu_2Cl_2 should reduce 0.003 to 0.005 g. of iron.

Standard Ferric Chloride Solution.—Dissolve 5 grams of standard iron wire in 100 ml. of hydrochloric acid (1 : 1), then 5 grams of potassium chlorate are added to oxidize the iron. Boil until all the free chlorine is driven off, then cool and make the solution up to two liters.

Method.—Dissolve one gram of drillings in 25 ml. of nitric acid (1 : 1), in a 300-ml. Griffin lip beaker, add 50 ml. of cold water and make strongly alkaline with ammonia. Boil a few minutes, filter and wash precipitate with hot water two or three times. The precipitate is redissolved in hot hydrochloric acid (1–3) to which a few drops of sulfurous acid are added. After the precipitate is dissolved, boil the solution a few minutes, add a few drops of nitric acid, let solution cool for 5 or 10 minutes, then make alkaline with ammonia, filter and wash with hot water. Repeat redissolving and ammonia precipitation. After final reprecipitation, dissolve the iron hydroxide in 30 ml. of hot hydrochloric acid (1–3) into a 24-oz. flask, cool and add 300 ml. of cold distilled water and titrate with a standard cuprous chloride solution, using 2 drops of a saturated solution of potassium sulfocyanate as inside indicator. The cuprous chloride solution is standardized each time before using, with standard ferric chloride.

NOTE.—If the ferric hydroxide is dissolved in dilute sulfuric acid and the iron reduced with zinc, the iron titrated with potassium permanganate is just as accurate as above method, providing 5 grams of the drillings are taken.

DETERMINATION OF SULFUR AND SILICON

Method.—Weigh 10 g. of drillings into an 800-ml. casserole, add 3 g. of $KClO_3$, cover and then add 200 ml. of concentrated HNO_3. Place on steam bath until action has ceased and then evaporate to dryness on the hot plate. Cool, add 50 ml. of HCl (sp.gr. 1.18) and again evaporate to dryness. Repeat this operation. Take up with 150 ml. of water, add 8 ml. of HCl (sp.gr. 1.18), heat to boiling, filter and wash, taking care that the filtrate and washings do not exceed 300 ml. in volume. Reserve the residue. Heat the filtrate to boiling, add 25 ml. of 20% $BaCl_2$ solution, and allow to stand in a warm place over night. Filter through a small double ashless filter paper and wash with very dilute HCl, and finally with hot water. Ignite in a small platinum crucible and then heat to bright redness for twenty minutes. Cool and weigh as $BaSO_4$. Multiply by 0.13735 for sulfur.

Transfer the residue to a weighed platinum crucible, dry, ignite and weigh as SiO_2. Multiply by 0.4672 for silicon.

Run a blank analysis on the chemicals used. If this blank amounts to 0.004 g., obtain fresh reagents and repeat the analysis.

Run in duplicate.

Determination of Manganese

Solutions Required. *Ferrous Ammonium Sulfate.*—35.6 grams per liter. Add about 1 ml. of sulfuric acid. One ml. equals 0.001 g. of Mn.

Potassium Permanganate.—2.90 grams per liter. One ml. equals 1 ml. of ferrous ammonium sulfate.

The ferrous ammonium sulfate solution changes rapidly, therefore, it is standardized against permanganate every day. Run 25 ml. of ferrous ammonium sulfate solution into a flask which contains a sample that has been titrated, then titrate to a faint pink with permanganate. This gives the value in permanganate of the ferrous ammonium sulfate.

Method.—Dissolve one gram of drillings in 10 ml. of concentrated nitric acid in a No. 2 tall 250 ml. beaker. Add 30 ml. of warm water and add about 0.5 g. of sodium bismuthate, heat a few minutes, then add enough sulfurous acid to clear the solution and boil until nitrous oxide is all driven off. Cool to about 15° C., add an excess of sodium bismuthate and let stand a few minutes. Filter through asbestos felt on a Gooch crucible into a 500 ml. Erlenmeyer suction flask; apply suction gently, wash with 3% nitric acid. Run into the flask a measured amount of ferrous ammonium sulfate solution and titrate the excess at once with standard potassium permanganate, deducting 0.5 ml. of permanganate, which is used in neutralizing the color of copper and nickel solution. The number of ml. of permanganate used less 0.5 ml. is subtracted from the original amount of ferrous ammonium sulfate taken and the remainder multiplied by 0.001 gives the per cent of manganese.

Determination of Carbon

The usual carbon combustion apparatus is used with a platinum combustion tube. In addition to the usual absorption train there is placed next to the platinum combustion tube a 5 inch " U "-tube filled with glass beads and moistened with chromic acid solution, with a loose plug of glasswool in the forward end. This serves to oxidize any sulfurous anhydride and to absorb the sulfuric anhydride formed from the sulfur in the drillings during combustion. This tube is washed out daily and fresh glasswood inserted. The forward end of the platinum combustion tube contains a plug of loosely wound platinum gauze, 5½ inches long, completely filling the bore of the tube and a similar roll 2 inches long, fitted with a loop is pushed in after the boat.

Fill the alundum boat with ignited alumina and make a " V "-shaped depression in the middle with a spatula, pressing the material against the sides of the boat. Ignite the boat and its contents strongly to expel any carbon dioxide present and burn off any carbonaceous matter that the alumina may contain. Weigh out 3 g. of the drillings which have been broken down so as to pass through a 10-mesh sieve and transfer it to the boat.

The absorption is made in potassium hydroxide (sp.gr. 1.27) placed into a Geissler potash bulb or with " Ascarite " contained in a Schwartz drying tube, with a calcium chloride tube attached. Burn the carbon by starting a slow current of oxygen and lighting one of the burners at the forward end of the tube, and as soon as the tube is red hot increase the heat slowly by lighting the other burners. The valve controlling the supply of oxygen must be regulated so as to keep a slow current of gas passing through the absorption apparatus at all

times, and not to exceed three bubbles in a second. Monel Metal containing manganese, or high in silicon, is burned at a temperature between 1125° C. and 1200° C., for twenty minutes.

Analysis of Aluminum and its Alloys.—See Chapter on Aluminum, Volume I.

Analysis of Beryllium-Copper Alloys.—See Chapter on Beryllium, Volume I.

Analysis of Magnesium and its Alloys.—See Chapter on Magnesium, Volume I.

TIN BASE AND LEAD BASE ALLOYS

ANALYSIS OF ALLOYS OF LEAD, COPPER, ANTIMONY AND TIN [11]

These methods apply particularly to white metal-bearing alloys [12] (known commercially as " Babbitt Metal ") and to similar lead and tin base alloys.

Two sets of methods are here given. The first method is somewhat slow but is recommended as giving the more accurate results where the analysis of these alloys is of comparatively infrequent occurrence. The second method is rapid and is suitable for control work, giving good results after the analyst has become familiar with it.

GENERAL METHODS [13]

A. DETERMINATION OF LEAD, COPPER, ANTIMONY AND TIN

Determination of Lead

Solutions Required. *Mixed Acid.*—Dissolve 20 g. of KCl in 500 ml. of water, add 400 ml. of HCl (sp.gr. 1.18), mix and add 100 ml. of HNO_3 (sp.gr. 1.42).

Alcohol-Hydrochloric Acid Mixture.—Mix 400 ml. of 95% ethyl alcohol and 100 ml. of HCl (sp.gr. 1.18).

Acid Ammonium Acetate.—To 500 ml. of NH_4OH (sp.gr. 0.90), add 500 ml. of water and then acetic acid (80%), until neutral to litmus; then add sufficient acetic acid to make the solution 2% acid with acetic (80%).

Method.—Dissolve 1 g. of the finely divided alloy by boiling in 70 to 100 ml. of " mixed acid " solution in a covered beaker. Add more " mixed acid " if a complete solution of the alloy is difficult to obtain, and continue boiling until evaporated to about 50 ml. Add 5 ml. of HCl (sp.gr. 1.18), cool in ice water until the bulk of $PbCl_2$ has crystallized out, then add slowly, with constant stirring, 50 ml. of alcohol (95%), continue stirring for a few minutes and

[11] A. S. T. M. Methods of Chemical Analysis of Metals, p. 184, December, 1936.
[12] For Specifications for Babbitt Metal, see 1936 A. S. T. M. Standards, Part I, p. 700.
[13] G. W. Thompson's Method, J. Chem. Ind., 15. 179 (1896).

cool in ice water for 10 minutes. Add 50 ml. more alcohol from a pipette, allow to stand in ice water for 20 minutes and filter through 9 cm. paper into an 800-ml. beaker. Wash by decantation three times with alcohol-hydrochloric acid mixture and finally wash the paper twice with the same mixture. Wash the $PbCl_2$ from the paper back into the beaker; wash paper several times with hot water, catching washings in beaker with the bulk of the chloride. Finally wash paper with hot acid ammonium acetate solution. Heat until all $PbCl_2$ is dissolved. Add 15 ml. of saturated solution of $K_2Cr_2O_7$; heat until precipitate is of good orange color; filter on weighed Gooch crucible; wash with water, alcohol and ether; dry at 100° C. and weigh. Calculate percentage of lead by the empirical factor 63.75.

NOTES.—1. With proper manipulation, the $PbCl_2$ should contain consistently all but 0.003 g. of lead. When, however, the lead content is low as in the high tin Babbitts, it is not necessary to use 70 to 100 ml. of mixed acid or to add alcohol after solution of the alloy. In such cases, weigh the alloy directly into a 600-ml. beaker, add about 15 ml. of HCl (1 : 1) warm, and then add HNO_3 (sp.gr. 1.42), a little at a time, until the alloy is dissolved and the tin completely oxidized.

2. During the heating of the acid ammonium acetate to dissolve the $PbCl_2$, the solution should remain perfectly clear, any turbidity indicating the presence of tin or antimony, as even 1 mg. of tin or antimony will cause a slight but distinct turbidity.

DETERMINATION OF COPPER AND ANTIMONY

Solutions Required.—***Potassium Hydroxide.***—Dissolve 100 g. of KOH in 500 ml. of water.

Potassium Cyanide.—Dissolve 3.5 g. of KCN in 1800 ml. of water and standardize against copper of known purity.

Sodium Thiosulfate.—Dissolve 24.8 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 1000 ml. of water, and allow to stand for 24 hours. Standardize against Antimony Metal c.p., using same quantity of reagents and same procedure as under (*c*) Determination of Antimony.

Method.—See " Determination of Lead."

Evaporate the filtrate from $PbCl_2$ filtration by boiling in the loosely covered 800-ml. beaker, and finally take to dryness on a water-bath. Add 10 ml. of KOH solution and after a few minutes add 20 ml. of 3% H_2O_2. Add more KOH, if solution is acid, until an alkaline reaction is shown by litmus paper. Heat on the water-bath for 20 minutes, add 10 g. of ammonium oxalate, 10 g. of oxalic acid, and 200 ml. of water and heat to boiling. Pass in H_2S for 45 minutes with solution near boiling; filter at once; and wash precipitate with hot dilute solution of oxalic acid saturated with H_2S, catching washings with filtrate.

Wash the precipitate of copper and antimony sulfides from the filter paper back into the beaker with the least amount of water possible; treat with 10 ml. of KOH solution; heat on water-bath until the undissolved matter is distinctly black, filter through same paper into a 500-ml. Erlenmeyer flask. Wash the precipitate with hot water containing a small amount of K_2S.

(*a*) *Determination of Copper by Potassium Cyanide Titration*

Dry and ignite the precipitate with paper in a small casserole, dissolve in nitric acid (sp.gr. 1.42), boil to expel nitrous fumes, neutralize with Na_2CO_3, add a few drops of NH_4OH and titrate with standard KCN solution.

(b) *Determination of Copper by Electrolytic Method*

See " Determination of Copper by Potassium Cyanide Titration."

Dry and ignite the sulfide precipitate in a small casserole, dissolve in 10 ml. of HNO_3 (sp.gr. 1.42), boil until oxides of nitrogen are expelled and add 50 ml. of distilled water. Transfer to a tall 200-ml. beaker, wash out casserole, add 5 ml. of H_2SO_4 (sp.gr. 1.84) and determine copper by electrolysis. See " Analysis of Manganese Bronze."

NOTES.—1. On filter after heating with KOH solution, the copper remains as sulfide with a small amount of lead sulfide which failed to be precipitated as chloride. If it is desired to determine this lead, it can be done by separation from the copper by ordinary methods.

2. If the amount of antimony and copper is small (less than 10 mg.), the lead which failed to be precipitated as chloride may also fail to come down as sulfide on passing H_2S through the oxalic solution. It will remain in the filtrate from the sulfides and be deposited electrolytically with the tin on the cathode. This can be prevented by adding an oxalic acid solution of a pure antimony salt containing about 100 mg. of antimony just before passing H_2S. In this case antimony must be determined on a separate portion. (See "Determination of Antimony in Solder," General Method.)

3. If the amount of copper present is from 8 to 10 mg. or more, it should be determined by the electrolytic method. In this case, the small amount of lead precipitated as sulfide with the copper is deposited on the anode as PbO_2 and may be weighed, calculated to lead by factor 0.8662 and added to that obtained under "Determinations of Lead."

(c) *Determination of Antimony*

See " Determination of Copper by Potassium Cyanide Titration."

Add 50 ml. of HCl (sp.gr. 1.18) to the KOH solution of antimony sulfide, and boil down to small volume until all arsenic has been expelled as arsenious chloride.

Add 25 ml. of HCl (sp.gr. 1.18) and 1 g. of $KClO_3$ and boil until colorless. Filter into a 500-ml. Erlenmeyer flask, through glass wool if sulfur has separated, wash out original flask with HCl (sp.gr. 1.18), cool, add 1 g. of KI, 1 ml. of CS_2, and titrate with standard thiosulfate solution.

NOTES.—1. When arsenic is present to the extent of 0.3%, the addition of 50 ml. of HCl (sp.gr. 1.18) to the KOH solution and subsequent boiling may not completely expel the arsenic. In such case add a gram or two of sodium thiosulfate and repeat with the addition of HCl and boiling.

2. If sulfur is present it will dissolve in the CS_2 and impart a color to the indicator which interferes with the reading of the end-point. To eliminate this condition titrate with the $Na_2S_2O_3$ solution to within 0.5 ml. of the end-point, pour the solution into a clean flask, add the CS_2 and continue the titration.

DETERMINATION OF TIN

Apparatus for Electrolysis. *Electrodes.*—See "Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

Platinum wire spiral anodes.

Method.—See " Determination of Copper and Antimony."

Concentrate the filtrate and washings from the precipitated sulfides, if necessary, to a volume of 200 ml. and add 5 g. more of oxalic acid in case the amount of tin is over 0.5 g. Electrolyze until the solution reacts alkaline, using a current of about 0.5 ampere. Remove the cylinder; wash twice with distilled water and once with 95% ethyl alcohol; dry at 110° C. and weigh.

NOTE.—1. If the electrolysis is carried out over night, it will usually be found by morning that the solution has become alkaline and it may be taken for granted that the tin has all been precipitated on the cathode. The best results are obtained by regulating the current, or the time, so as to render the solution alkaline only a very short time before the cathode is to be removed. The anode should touch the bottom of the beaker to insure proper agitation of the electrolyte. The cathode should be 0.25 inch above.

2. Appreciable amounts of nickel, zinc and iron should not be present.

B. Determination of Arsenic

Solutions Required. *Ferric Chloride.*—Solution of specific gravity 1.43.

Ammonium Carbonate.—Dissolve 75 g. in 500 ml. of water.

Method.—Weigh 1 g. of sample into a 250-ml. distillation flask and add 10 ml. of $FeCl_3$ solution, 60 ml. of HCl (sp.gr. 1.18), 20 ml. of water and 5 g. of KCl. Connect the flask with a condenser, heat slowly until solution is complete and boil down to as small a volume as possible, catching distillate in a tall 400-ml. beaker. Cool flask, add 50 ml. HCl (sp.gr. 1.18) and redistill as before, catching distillate in same beaker. Cool distillate and pass H_2S through for one hour, allow to settle and filter the arsenious sulfide on a Gooch crucible. Wash twice with HCl (1 : 4), four times with cold water, three times with alcohol and four times with CS_2. Dry at 110° C. for 10 minutes, and weigh after cooling. Dissolve the arsenious sulfide with $(NH_4)_2CO_3$ solution, wash thoroughly with water, dry for 30 minutes at 110° C. and reweigh after cooling. The difference in weights multiplied by 0.6091 gives the percentage of arsenic.

RAPID METHODS FOR CONTROL WORK[14]

A. DETERMINATION OF LEAD AND COPPER

Solutions Required. *Lead Acid.*—See "Determination of Lead as Sulfate, Analysis of Manganese Bronze."

Dilute Alcohol for Washing.—Mix equal parts of denatured alcohol and distilled water.

Method

(*a*) *Determination of Lead*

In a covered 300-ml. Erlenmeyer flask dissolve 1 g. of the alloy in 20 ml. of H_2SO_4 (sp.gr. 1.84); heat the solution nearly to boiling until the metal is completely decomposed and the $PbSO_4$ is white (this may take 30 minutes or more) and finally boil for several minutes. Allow to cool, but not below 60° C., and then add slowly 50 ml. of water while the solution is agitated. Heat to boiling for several minutes in order to insure complete solution of antimony sulfate. Allow the $PbSO_4$ to settle out until the solution is clear, not letting the temperature fall below 60° C. If the liquid does not clear quickly, it must be heated longer. When clear, pour the solution through a weighed porcelain Gooch crucible with asbestos mat, decanting the solution as completely as possible without allowing more than a very small amount of $PbSO_4$

[14] See "The Analysis of Lead, Tin, Antimony and Copper," by D. J. Demorest, J. Ind. and Eng. Chem., **5**, 842 (1913); "Rapid Analysis of Alloys for Tin, Antimony and Arsenic," by F. A. Stief, J. Ind. and Eng. Chem., **7**, 211 (1915); and W. B. Price and R. K. Meade, "Technical Analysis of Brass," p. 182, John Wiley and Sons, N. Y., 1917.

to go over into the crucible. Now add 10 ml. more of H_2SO_4 (sp.gr. 1.84) to the $PbSO_4$ in the original flask, and boil for several minutes. Cool, add slowly 30 ml. of water, and again heat to boiling for a few minutes; allow the solution to cool to about 60° C. and completely transfer the $PbSO_4$ to the Gooch crucible. Wash with lead acid, retaining the filtrate and these washings for the copper determinations. Remove the beaker containing these solutions and wash out the lead acid with dilute alcohol; set the Gooch crucible inside a porcelain crucible; dry and ignite for five minutes at the full heat of a Tirrill burner; cool and weigh as $PbSO_4$, which contains 68.33% lead.

(b) Determination of Copper

To the filtrate from the $PbSO_4$, which contains the copper and which has been transferred to an Erlenmeyer flask, add NH_4OH (sp.gr. 0.90) until the solution is slightly alkaline; then add 2 ml. of H_2SO_4 (sp.gr. 1.84); heat nearly to boiling; add 2 g. of Na_2SO_3 and when this is entirely dissolved add 1 g. of KCNS dissolved in 10 ml. of water. Shake well and allow the precipitated CuCNS to settle for one hour while the solution is kept hot. Filter on a close filter paper, wash with cold water and ignite paper and precipitate in a porcelain crucible. Proceed by one of the two following methods:

(1) Dissolve in HNO_3 (sp.gr. 1.42), add 5 ml. H_2SO_4 (sp.gr. 1.84); evaporate until fumes of H_2SO_4 are evolved. Dilute to about 100 ml. with distilled water. Add 1.5 ml. of HNO_3 (sp.gr. 1.42) and determine copper by electrolysis. See the "Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

(2) Dissolving the ignited precipitate in HNO_3 (sp.gr. 1.42), as in (1); boil to expel nitrous fumes, neutralize with Na_2CO_3 and determine volumetrically with cyanide as in A of "General Method."

NOTE.—If the amount of copper is very small it may escape detection by this method, in which case it should be determined as in A of "General Method."

B. DETERMINATION OF ARSENIC, ANTIMONY AND TIN

Apparatus. ***Arsenic Still.***—A condenser is made from glass tubing in the form of a letter S, about 18 in. long and ½ in. in inside diameter, tapering to about ¼ in. at the upper end and to about ⅛ in. at the lower end. One curve is nearly filled with water, and is submerged in cold water in a 500-ml. beaker. The lower end dips into about 75 ml. of water in a 300-ml. beaker and the upper end is connected by a delivery tube with a 300-ml. Florence flask, closed with a rubber stopper which is fitted with a delivery tube and with a thermometer reaching to about 1 in. above the surface of the liquid in the flask.

Solutions Required. ***Iodine.***—Dissolve 10.7 g. of iodine in 50 ml. of distilled water which contains 20 g. of KI in solution and dilute to 1000 ml. with distilled water. Standardize against pure tin having exactly the same conditions for titration as are specified for the analysis of the alloy. Each milliliter is equivalent to approximately 0.00500 g. of tin or 0.00315 g. of arsenic.

Potassium Permanganate.—Dissolve 2.7 g. of $KMnO_4$ in distilled water, filter through asbestos, and dilute to 1000 ml. with distilled water. Standardize against pure antimony having exactly the same conditions for titration as are

specified for the analysis of the alloy. Each milliliter is equivalent to approximately 0.00500 g. of antimony or 0.00465 g. of iron.

Ferrous Ammonium Sulfate.—Dissolve 12.4 g. of ferrous ammonium sulfate crystals in 950 ml. of distilled water and add 50 ml. of H_2SO_4 (sp.gr. 1.84).

Starch.—To 1000 ml. of boiling water add a cold suspension of 6 g. of starch in 100 ml. of distilled water; cool, add a few drops of chloroform and mix thoroughly.

(*a*) *Determination of Arsenic*

Method.—In a 300-ml. Florence flask, dissolve 0.5 g. of the alloy in exactly 8 ml. of H_2SO_4 (sp.gr. 1.84). The metal must be finely divided, preferably in the form of thin foil-like shavings, although sawings or very fine drillings may be used. Heat the solution to boiling; cool, add about 5 ml. of water and a bulk of about 0.5 ml. of clean granulated pumice stone and boil the covered solution very gently for about five minutes, or until the strong odor of SO_2 can no longer be detected. Finally, being careful to have 5 ml. of water present, cool the solution to about 18° C. and cautiously add 20 ml. of HCl (sp.gr. 1.18). Insert in the flask a rubber stopper fitted with a thermometer and delivery tube and connect the delivery tube with the " S " condenser. Heat the solution to gentle boiling for from 10 to 15 minutes, keeping the vapor temperature at 107° C. for at least 5 minutes. Wash out the condenser into a 300-ml. beaker and add an excess of about 2 g. of $NaHCO_3$. Bring the volume of the solution to about 200 ml.; warm to about 27° C., add 5 ml. of starch solution and titrate with standard iodine solution to the appearance of a deep blue color.

NOTE.—A blank determination should be made on corresponding amounts of reagents treated as above, and the results should be corrected accordingly.

(*b*) *Determination of Antimony*

Cool the solution which remains in the flask after the arsenic distillation; add about 130 ml. of cold, recently-boiled distilled water to which has been added about 3 ml. of HCl (sp.gr. 1.18) and titrate with standard $KMnO_4$ solution to the appearance of a decided permanent pink color. From a burette add an excess of standard ferrous ammonium sulfate solution until the pink color is discharged and then titrate with standard $KMnO_4$ solution to the reappearance of a pink color.

(*c*) *Determination of Tin*

If the sample does not contain 14% (or 0.07 g.) of antimony, add enough dissolved $SbCl_3$ to the solution to bring the contents of antimony up to about 0.07 g. for the purpose of insuring perfect reduction of the tin and uniform conditions for the titration. Then add exactly 6 ml. of H_2SO_4 (sp.gr. 1.84) and 60 ml. of HCl (sp.gr. 1.18) and add about 6 in. of clean, soft No. 14 pure iron wire cut into 2 in. lengths and cleaned with dilute HCl just before using. Boil gently for 30 minutes, add about 6 in. more wire and boil 30 minutes longer. Remove from heat, close flask loosely with a rubber stopper and allow about two minutes for all air to be expelled by hydrogen and acid vapors. Close flask tightly and quickly place it in cold water, cooling the solution to about 20° C. Transfer the solution quickly to a 500-ml. beaker (leaving the iron

wires in the flask) and rinse flask and contents with 150 ml. of cold, recently-boiled distilled water. Add rinsings to main solution in the beaker, bring final volume to about 300 to 350 ml., add 5 ml. of starch solution and titrate quickly with standard iodine solution to the appearance of a strong blue color.

NOTES.—A blank determination should be made on corresponding amounts of reagents treated as above, and the results should be corrected accordingly.

If the copper content of the alloy is as high as about 3% or over, it prevents a good end-point in the tin titration when the tin percentage is low. Under such conditions, just before titrating, add about 1 g. of KI crystals, stir until nearly dissolved and titrate immediately. If allowed to stand too long at this point, trouble may be encountered due to the precipitation of some of the other constituents.

Other forms of pure iron may be employed, but the wire as above specified has been found convenient.

For accurate work it is desirable to reduce and titrate the solution of tin in an atmosphere of CO_2.

THE DETERMINATION OF IMPURITIES IN TIN BASE AND LEAD BASE ALLOYS [15]

General Considerations.—The impurities that are usually present in tin base and lead base alloys vary from 0.5% to traces. The following methods are given on the assumption that an impurity does not exceed 0.10%. When an impurity is present to a greater extent, a smaller amount of sample may be taken.

THE DETERMINATION OF LEAD, BISMUTH, IRON, ALUMINUM AND NICKEL IN TIN BASE BEARING METAL

Determination of Lead

Solutions Required. ***Potassium Hydrosulfide Stock Solution.***—Weigh 200 g. of KOH into an 1100-ml. beaker, dissolve in about 800 ml. of distilled water and pass H_2S for about one hour. Make up to a volume of 2000 ml. with distilled water, mix and allow to stand over night. Filter off portions as required for use.

Potassium Hydrosulfide Wash Solution.—Mix one part of the potassium hydrosulfide stock solution with two parts of distilled water.

Lead Acid.—See "Determination of Lead as Sulfate, Analysis of Manganese Bronze."

Acid Ammonium Acetate.—See "Determination of Lead, Analysis of Alloys of Lead, Copper, Antimony and Tin" under General Methods.

Method.—Weigh 5 g. of the sawings into a 600-ml. beaker, add 30 ml. of HCl (sp.gr. 1.18), warm on a hot plate and add HNO_3 (sp.gr. 1.42), a few drops at a time, until the alloy is dissolved and the tin is completely oxidized. Dilute to a volume of 100 ml. with cold water and make strongly alkaline with a cold saturated solution of KOH. Avoid a large excess of the KOH solution. Immediately add 70 ml. of the potassium hydrosulfide stock solution, stir and allow to stand in a warm place until the precipitate settles and the supernatant solution is a clear lemon yellow. Filter and wash with the warmed potassium hydrosulfide wash solution.

[15] Methods of the National Lead Company Research Laboratories.

Throw the filter paper and precipitate back into the original beaker, add 5 ml. of HNO_3 (sp.gr. 1.42), heat until the paper is pulped and the sulfide dissolved, add 40 ml. of lead acid and evaporate to fumes of H_2SO_4. Just before the solution begins to fume it will become dark colored due to the action of the H_2SO_4 on the filter paper. At this point add a drop or two of HNO_3 (sp.gr. 1.42) to the hot solution and continue to fume. Repeat the addition of HNO_3 until the solution shows no brown coloration even upon strong fuming. Cool, add a few ml. of water and take to fumes a second time. Again add a few ml. of water and fume. Finally cool, add 35 ml. of water, bring to boiling, cool, and allow to stand several hours. Filter and wash with lead acid.

Dissolve the $PbSO_4$ with 30 ml. of hot ammonium acetate solution, wash with hot water, dilute to a volume of 150 ml., bring to boiling, add 10 ml. of a saturated solution of $K_2Cr_2O_7$ and allow to stand in a warm place several hours. Filter on a weighed porcelain gooch crucible and wash several times with hot water and once with alcohol. Dry at 110° C. for one hour. Cool and weigh as $PbCrO_4$. Multiply by 0.6375 for lead.

Accuracy.—Duplicate determinations should check within 0.008% of lead.

Note.—In preparing the Gooch crucible it is advisable to fit a small filter paper in the bottom of the Gooch crucible before adding the asbestos and treat exactly as in the determination.

Determination of Bismuth

Method.—Dissolve 10 g. of sawings with 50 ml. of HCl (sp.gr. 1.18) and sufficient HNO_3 (sp.gr. 1.42) to oxidize the tin, dilute to a volume of 150 ml., make alkaline with a saturated solution of KOH, add 80 ml. of the KSH stock solution, stir, allow to stand, filter and wash with the KSH wash solution. (See "Determination of Lead.")

Wash the precipitate back into the beaker, place under the funnel and pour through the filter 15 ml. of hot HNO_3 (1 : 2). Bring to boiling, filter through the same paper and wash with hot water. If a black residue still remains, transfer to a small porcelain crucible, dry, ignite at a low heat, dissolve in 2 ml. of HNO_3 (sp.gr. 1.42) and transfer to the main solution. Evaporate to a volume of 50 ml. and allow to stand in a warm place for one hour. If a precipitate of H_2SnO_3 forms, filter and wash with hot HNO_3 (1 : 50). Discard the residue.

Make the solution just neutral with NH_4OH (1 : 2), add 5 ml. of HCl (1 : 9) in excess, dilute to a volume of 400 ml. with hot water and allow to stand in a warm place at least two hours, preferably over night. Filter on a weighed porcelain Gooch crucible, wash several times with hot water, once with alcohol, dry at 110° C. for one hour, cool and weigh as BiOCl. Multiply by 0.8024 for bismuth.

Accuracy.—Duplicate determinations should check within 0.005% of bismuth.

Notes.—1. When a relatively large amount of a lead base alloy or a tin base alloy containing considerable lead is dissolved in a HCl solution, lead chloride will separate out before the alloy is dissolved, if insufficient solution is present, and retard further solvent action. For the solution of alloys containing lead and subsequent procedure see "Determination of Antimony, Zinc and Copper in Solder."

2. If a precipitate of H_2SnO_3 forms when the sulfides are dissolved in HNO_3, antimony may be present in solution, and precipitate out with the BiOCl. In that case,

filter the BiOCl on a paper, dissolve in 10 ml. of hot HCl (1 : 1), wash, dilute to 100 ml., pass H_2S, filter, wash, treat the sulfides, with 10 ml. of the KSH stock solution mixed with an equal quantity of water, filter and wash. Proceed as described above.

3. See Note under "Determination of Lead."

Determination of Iron

Method.—Dissolve 12.5 g. of alloy as described under "Determination of Bismuth." Add about 2 g. of KCl and evaporate to near dryness. Add 20 ml. of HCl (sp.gr. 1.18), dilute to 50 ml. with water, bring to boiling and pass H_2S. As the sulfides begin to form, keep adding hot water from time to time until the volume of solution is finally brought up to 400 ml. Continue passing H_2S for 30 minutes. Transfer to a 500-ml. graduated flask, cool to room temperature, make up to the mark with a 2% solution of HCl through which H_2S has been passed, mix and filter off 400 ml. through a dry paper discarding the first 15 or 20 ml. of solution.

Boil the filtrate to expel H_2S, add 3 ml. of HNO_3 (sp.gr. 1.42) to oxidize the iron, make just alkaline with NH_4OH (sp.gr. 0.9), using methyl red as an indicator, boil for two minutes, filter and wash several times with a 2% solution of NH_4Cl, and once with hot water. (The filtrate may be used for zinc. See "Determination of Zinc in Solder.") Dissolve the precipitate from the filter with 15 ml. of H_2SO_4 (1 : 4), wash with hot water and evaporate to fumes of H_2SO_4. Cool, add 25 ml. of water, bring to boiling, cool and allow to stand for any lead to separate that may not have been precipitated by the H_2S. Filter and wash with cold dilute H_2SO_4 (1 : 9). To the filtrate add a slight excess of a strong solution of $KMnO_4$, pass through a Jones reductor and titrate with approximately 0.006 N $KMnO_4$. (See "Determination of Iron, Analysis of Manganese Bronze.")

Accuracy.—Duplicate determinations should check within 0.003% of iron.

Notes.—1. See Note 1 under "Determination of Bismuth," and "Determination of Zinc, Determination of Antimony, Zinc and Copper in Solder."

2. If iron only is desired, the solution may be made slightly alkaline and allowed to stand an hour or so in a warm place. The addition of methyl red may be dispensed with.

Determination of Aluminum

Apparatus Required. ***Anodes.***—Platinum wire spirals.

Cathodes.—The cathode is metallic mercury contained in a glass receptacle (Fig. 182) in which has been fused at *A* a small piece of fine platinum wire looped at the outer end. Contact is made by means of a piece of copper wire. About 12 ml. of mercury is used forming a column about 1.5 inches high. The apparatus will conveniently hold, exclusive of the mercury, 125 ml. of solution.

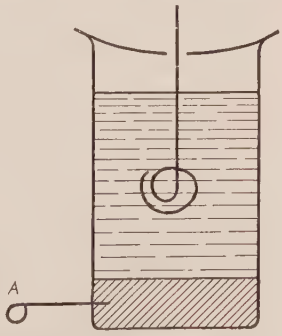

Fig. 182. Apparatus for Determination of Aluminum.

Method.—Proceed exactly as in "Determination of Iron" up to the point where any lead that may not have been precipitated as a sulfide has been separated as a sulfate.

Make the filtrate just neutral with NH_4OH (1 : 2) and then acid with 10 ml. of H_2SO_4 (1 : 9) in excess. Dilute to a volume of 80 ml., transfer to the

receptacle containing the mercury as cathode, and electrolyze over night using a current of 0.5 ampere. Transfer the electrolyte to a 400-ml. beaker, wash the mercury with water, combine electrolyte and washings, add 5 g. of NH_4Cl, make just neutral with NH_4OH using methyl red as an indicator, boil for two minutes, filter and wash with hot water. Ignite in a weighed porcelain crucible at first over a low, then over a strong Bunsen flame. Cool and weigh as Al_2O_3. Multiply by 0.529 for aluminum.

Accuracy.—Duplicate determinations should check within 0.003% of aluminum.

NOTES.—1. See Note 1 under "Determination of Bismuth."

2. Phosphorus, if present, will interfere. For its correction see "Determination of Aluminum, Analysis of Manganese Bronze," Method (*a*).

DETERMINATION OF NICKEL

Method.—Proceed exactly as in " Determination of Iron " up to the point where 400 ml. of solution has been filtered off from the sulfides.

Boil to expel H_2S, add 3 ml. of HNO_3 (sp.gr. 1.42) to oxidize iron, evaporate to a volume of about 100 ml., add 10 ml. of a 20% solution of sodium potassium tartrate, nearly neutralize with NH_4OH (sp.gr. 0.9), heat nearly to boiling, add 10 ml. of a 1% solution of dimethylglyoxime and then NH_4OH in slight excess. Allow to stand in a warm place at least 30 minutes, filter on a weighed Gooch crucible and wash with 1% solution of NH_4OH. Dry at 110° C. for two hours. Cool and weigh as $NiC_8H_{14}N_4O_4$. Multiply by 0.2032 for Nickel (see " Determination of Nickel, Analyses of Bronze Bearing Metal ").

Accuracy.—Duplicate determinations should check within 0.001% of nickel.

NOTES.—1. The filtrate from the iron and aluminum separation with NH_4OH may be used for the determination of nickel in which case the addition of sodium potassium tartrate is unnecessary.

2. See Note under "Determination of Lead."

DETERMINATION OF ANTIMONY, ZINC AND COPPER IN SOLDER [16]

(ALLOY OF LEAD AND TIN)

DETERMINATION OF ANTIMONY [17]

A. General Method

Solutions Required. ***Mixed Acid.***—Mix 400 ml. of HCl (sp.gr. 1.18) and 500 ml. of water and then add 100 ml. of HNO_3 (1.42).

Potassium Hydroxide Solution.—Dissolve 100 g. of KOH in 500 ml. of water.

Copper Solution.—Dissolve 2.0 g. of $CuSO_4 \cdot 5H_2O$ in 500 ml. of water.

KSH Stock Solution.—See " Determination of Lead, etc., in Tin Base Bearing Metal."

[16] Methods of the National Lead Company Research Laboratories.

[17] See "Specifications for Solder Metal," 1936 Book of A. S. T. M. Standards, part I, p. 695.

Potassium Iodide Solution.—Dissolve 20 g. of KI in 500 ml. of water.

Sodium Thiosulfate.—See " Determination of Lead, Analysis of Alloys of Lead, Copper, Antimony and Tin," General Methods.

Method.—Weigh 5 g. of the sawings into a 250-ml. beaker, add 150 ml. of the mixed acid and heat over a low flame on the hot plate. When $PbCl_2$ begins to form, decant the clear solution into a 400-ml. beaker, again add 150 ml. of the mixed acid to the undissolved alloy and continue heating until the solution is complete. Two 150 ml. additions of the mixed acid should suffice to completely dissolve the alloy without the formation of appreciable $PbCl_2$ in the hot solution. Combine the two solutions, add about 2 g. of KCl, evaporate to a volume of 100 ml., cool in ice water and separate the $PbCl_2$ by decantation, washing three times with cold HCl (1 : 2). Evaporate to a volume of 40 ml. Cool, allow to stand a few hours or preferably over night, decant the clear solution into a 600-ml. beaker, wash the $PbCl_2$ by decantation with cold HCl (1 : 2) pouring the washings through a small filter, evaporate the solution to near dryness, make just alkaline with KOH solution, add 12 g. of oxalic acid and 10 ml. of copper solution, dilute to a volume of 400 ml., bring to boiling, and pass H_2S for 45 minutes, keeping the solution hot and the volume constant during the passage of the H_2S. Filter and wash with a hot dilute solution of oxalic acid saturated with H_2S.

Wash the precipitate from the filter paper back into the beaker, add 10 ml. of KSH stock solution and 10 ml. of KOH solution, and digest on the water bath for 5 or 10 minutes. Filter through the same paper into a 500-ml. Erlenmeyer flask and wash with hot water containing a little of the KSH solution. Discard the residue.

Proceed exactly as in " Determination of Antimony, Analysis of Alloys of Lead, Copper, Antimony and Tin," General Methods.

Accuracy.—Duplicate determinations should check within 0.012% of antimony.

B. Rapid Method for Control Work

Solutions Required. *N/20 Potassium Permanganate Solution.*—Dissolve 1.58 g. of $KMnO_4$ in 1 liter of water. For its preparation and standardization see " Determination of Antimony, Analysis of Alloys of Lead, Copper, Antimony and Tin," Rapid Methods for Control Work.

Method.—Weigh 3 g. of the sawings into a 500-ml. Florence flask, add 20 ml. of H_2SO_4 (sp.gr. 1.84), place over a free flame and heat until completely decomposed. Cool, add 50 ml. of distilled water and boil down to a volume of 40 ml. If SO_2 is not completely expelled, dilute slightly and continue boiling until it is. The volume at this stage should be 35 to 40 ml. Cool, add 15 ml. of HCl (sp.gr. 1.18) and boil vigorously for five minutes. Add 200 ml. of cold water, immerse in cold tap water until the solution is cold and titrate with N/20 $KMnO_4$ solution to the first tinge of a permanent pink.

Run a blank determination on a mixture composed of pure tin and pure lead approximating the composition of the sample. Correct for same.

Accuracy.—Duplicate determinations should check within 0.01% of antimony.

NOTE.—The antimony content of the metals used for the blank should be known. The best brands of tin on the market may carry a small amount of antimony; the best brands of lead may carry as a maximum 0.004% of antimony.

Determination of Zinc

Solutions Required. *Citric Acid Solution.*—Dissolve 250 g. of the crystals in 500 ml. of water.

Standard Zinc Solution.—Dissolve exactly 0.1 g. of U. S. Bureau of Standards pure zinc in 5 ml. of HCl (sp.gr. 1.18) and dilute to exactly 1000 ml. with water.

Potassium Ferrocyanide Solution.—Dissolve 2 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ in 100 ml. of water.

Method.[18]—Weigh 6.25 g. of the sawings into a 250-ml. beaker and proceed exactly as in " Determination of Antimony " up to the point where the solution is evaporated to near dryness. Add 20 ml. of HCl (sp.gr. 1.18), dilute to 50 ml. with water, bring to boiling and pass H_2S, adding hot water from time to time during the passage of the H_2S until the volume is brought up to 400 ml. Continue passing H_2S for 30 minutes. Transfer to a 500-ml. graduated flask, cool to room temperature, make up to the mark with a 2% solution of HCl through which H_2S has been passed, mix and filter off 400 ml. through a dry paper discarding the first 15 or 20 ml. of solution.

To the filtrate add 5 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate fumes of H_2SO_4. Cool, add 35 ml. of water, bring to boiling, cool, and allow to stand. Filter and wash with cold dilute H_2SO_4 (1 : 9). Discard the residue. Bring the filtrate to boiling, add 3 ml. of HNO_3 (sp.gr. 1.42), add 2 g. of NH_4Cl, make slightly alkaline with NH_4OH (sp.gr. 0.9), again bring to boiling and allow to stand in a warm place for an hour or so. Filter and wash.

Boil the filtrate to expel NH_4OH, add 10 ml. of citric acid solution, dilute to a volume of 200 ml., again bring to boiling and cautiously add $CaCO_3$ in small portions at a time until about 1 g. of calcium citrate separates. Pass H_2S through the solution until cold and allow to stand several hours, part of the time on a water bath. Filter and wash with a 2% solution of ammonium thiocyanate.

Wash the precipitate back into the beaker with as little water as possible, set the beaker under the funnel and pour through the filter 15 ml. of HCl (1 : 1). Replace with a clean beaker, bring the solution to boiling, filter through the same paper and wash with hot water. Keep the volume below 100 ml. Reserve as solution No. 1. At the same time the sample is being run a blank determination should be carried along. Reserve as solution No. 2. Cool both solutions to room temperature.

Transfer solution No. 1 into a 100-ml. Nessler tube, add 2 ml. of the ferrocyanide solution, make up to mark and mix. Transfer solution No. 2 into another 100-ml. Nessler tube, add 2 ml. of the potassium ferrocyanide solution, make up to mark, mix and add the standard zinc solution, a few drops at a time, until the turbidities match. Mix between each addition of the standard. Comparison is best made by setting the tubes over a sheet of fine print and looking down the tubes. (See "Determination of Zinc, Tentative Methods of Chemical Analysis of Pig Lead.")

Accuracy.—Duplicate determinations should check within 0.001% of zinc.

[18] See "Determination of Small Quantities of Zinc," by M. Bodansky, J. Ind. and Eng. Chem., **13**, 696 (1921).

NOTE.—The turbidimetric test is very sensitive for amounts of zinc not exceeding 0.0005 g. If the sample contains over 0.01% of zinc take such an aliquot portion as will not contain more than this amount.

Determination of Copper

Solutions Required. *Standard KCN Solution.*—Dissolve 4 g. of KCN in 1000 ml. of water. Standardize against pure copper exactly as in the determination. Each ml. of the standard solution should equal about 0.001 g. of copper.

KSH Stock and Wash Solutions.—See "Determination of Lead, etc. in Tin Base Bearing Metal."

Method.—Weigh 5 g. of the sawings into a 250-ml. beaker and proceed exactly as in "Determination of Antimony" up to the point where the lead has been separated as $PbCl_2$. Dilute the filtrate to a volume of 150 ml., make alkaline with a saturated solution of KOH, add 70 ml. of KSH stock solution, stir, allow to settle, filter and wash with KSH wash solution. Throw the filter back into the beaker, add 5 ml. of HNO_3 (sp.gr. 1.42) and 5 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of H_2SO_4. Remove carbonaceous matter with HNO_3 (sp.gr. 1.42) and again fume. Cool, add 50 ml. of water, bring to boiling, cool, allow to stand, filter and wash with cold water. (See "Determination of Lead, Analysis of Lead, Bismuth, etc. in a Tin Base Bearing Metal.") Discard the residue.

Warm the filtrate, pass H_2S for 15 minutes, filter and wash with H_2S water. Wash the precipitate back into the same beaker, add 10 ml. of KSH stock solution, digest on the hot plate for a few minutes, filter through the same paper, and wash two or three times with KSH wash solution and twice with H_2S water.

Transfer the residue to a small porcelain crucible, dry, ignite, cool, add 2 ml. of HNO_3 (1 : 1) and evaporate to dryness. Cool, add 1 ml. of HNO_3 (1 : 1), neutralize with a saturated solution of sodium carbonate, add 4 drops of NH_4OH (sp.gr. 0.9) and titrate with standard KCN solution to the disappearance of the blue color.

Accuracy.—Duplicate determinations should check within 0.004% of copper.

NOTE.—For amounts of copper exceeding 0.010 g. weigh out a smaller charge or determine the copper electrolytically. (See "Determination of Copper, Analysis of Alloys of Lead, Tin, Antimony and Copper," General Methods.)

DETERMINATION OF TIN IN BATTERY PLATE METAL

(Alloy of Lead and Antimony)

Apparatus Required.—Insert in a No. 6 sulfur-free rubber stopper a bent outlet tube having an outside diameter of about 3.5 mm. and a capacity of about 12 ml. A bent pipette will answer for the purpose. When the stopper is inserted into the mouth of a 500-ml. Erlenmeyer flask the short end of the tube should just pass through the stopper while the other end should reach to a level ½ in. from the bottom of the flask and be 1 in. distant from it.[19]

[19] Craig, A., "Notes on Chemical Analysis," p. 114, The Chemical Publishing Co., 1924.

Solutions Required. *Standard Iodine Solution and Starch Indicator.*—See "Analysis of Alloys of Lead, Copper, Antimony and Tin," Rapid Methods for Control Work.

Sodium Bicarbonate Solution.—Dissolve 10 g. of $NaHCO_3$ in 100 ml. of recently boiled distilled water contained in a 150 ml.-beaker.

Method.—Weigh 5–10 g. of sawings into a 300-ml. cone flask, add 25–30 ml. of H_2SO_4 (sp.gr. 1.84) and heat on a bare hot plate until completely decomposed. Cool, add 100 ml. of water and 20 ml. of HCl (sp.gr. 1.18), introduce four pieces of iron and heat on the hot plate over a low flame until the iron is almost but not entirely dissolved. A reduction of 30 minutes should suffice. Filter off the precipitated metals through glass wool into a 500-ml. Erlenmeyer flask in which has been placed four pieces of iron and wash flask and funnel with hot water. The volume at this stage should be about 250 ml. Connect up the outlet tube and reduce as before. When reduction is complete, set the bicarbonate solution so that the free end of the outlet tube is immersed in it. When gas bubbles start to pass through the $NaHCO_3$ solution, remove both flask and beaker from the stove, allow to cool at room temperature for about 10 minutes and then cool the flask in cold tap water. Remove the outlet tube, withdraw the undissolved iron with a magnetized steel rod or file, wash both removed iron and rod with water, add 5 ml. of starch solution, and titrate with the standard iodine solution to the first tinge of blue.

Run a blank by treating 10 g. of lead sawings exactly as the alloy was treated and make a correction for same.

Accuracy.—Duplicate titrations should not disagree more than 0.1 ml.

NOTES.—1. Ordinary strap iron used for strapping shipping cases may be used for the tin reduction. Each piece should be 2 in. long and ½ in. wide, weigh about 2 g. and be free from grease, lacquer and rust.

2. The free end of the outlet tube should be kept immersed in the $NaHCO_3$ solution during the whole cooling operation.

ANALYSIS OF ZINC BASE DIE-CASTING ALLOY [20]

ALLOY OF ZINC, COPPER AND ALUMINUM [21]

A. DETERMINATION OF COPPER AND ALUMINUM

Electrodes for the Electrolysis of Copper.—See "Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

Apparatus for the Electrolytic Separation of Zinc.[22]—See "Determination of Aluminum, Determination of Lead, Bismuth, etc. in Tin Base Bearing Metal."

[20] Methods of the National Lead Company, Research Laboratories.

[21] For specifications, see 1935 Book of A. S. T. M. Tentative Standards, p. 369.

[22] See "Determination of Aluminum and Magnesium in Zinc Base Die Casting Alloys," by C. M. Craighead, J. Ind. and Eng. Chem., Anal. Ed., 2, 188 (1930).

Solutions Required. *Acidulated H_2S Wash Water.*—Dilute 10 ml. of H_2SO_4 (sp.gr. 1.84) to 500 ml. with water and pass H_2S for 10 minutes.

Method.—Weigh 4.0 g. of the sawings into a 300-ml. beaker, add 100 ml. of water and 15 ml. of H_2SO_4 (sp.gr. 1.84). (Add the acid in small doses.) When decomposition is complete, filter and wash with hot water. Hold the residue. Through the filtrate pass H_2S, filter and wash with acidulated H_2S wash water. Throw both filters into the beaker the filtration was made from, add 5 ml. of HNO_3 (sp.gr. 1.42) and 5 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of SO_3, adding a few drops of HNO_3 (sp.gr. 1.42) from time to time until the solution shows no evidence of a brown coloration. Finally cool, take up with 100 ml. of water, bring to boiling, add 3 ml. of HNO_3 (sp.gr. 1.42), wash into a 200-ml. lipless beaker, cool, dilute to a volume of 150 ml. and electrolyze over night with a current of 0.5 amperes. Weigh as metallic copper Run in duplicate.

Boil the filtrate from the CuS separation to expel H_2S, oxidize any iron present with a few ml. of H_2O_2 and continue boiling until the solution has attained a volume of about 75 ml. Cool, transfer to the receptacle containing the mercury and electrolyze over night with a current of 1.5 amperes.

Transfer the electrolyte to a 400-ml. beaker, wash the anode and the mercury with water, combine electrolyte and washings, add 5 g. of NH_4Cl make just neutral with NH_4OH (1 : 1) using methyl red as an indicator, boil for 2 minutes, filter, wash, ignite over a blast to constant weight and weigh as Al_2O_3. Multiply by 0.5291 for Al. Run in duplicate.

Notes.—1. Should the copper content of the alloy be low (0.1% or less) the determination may be made by a cyanide titration.

2. If the separation of zinc is incomplete a second separation of the $Al(OH)_3$ will have to be made. The presence of zinc may readily be detected by passing H_2S through a portion of the filtrate.

3. A small amount of iron may be present with the Al_2O_3. In such case, triturate, add 5 ml. of HCl (sp.gr. 1.18), evaporate to dryness, take up with 5 ml. of HCl (sp.gr. 1.18), transfer to a 100-ml. graduated flask, make up to the mark, mix, tap off 25 ml. into a 100-ml. graduated Nessler tube, add 2 ml. of NH_4CNS (1 : 5), make up to the mark, mix and match against a standard solution of iron (1 ml. = 0.0001 g. of iron) under similar conditions.

B. DETERMINATION OF MAGNESIUM

Method.—Weigh 10 g. of the sawings into a 400-ml. beaker, add 100 ml. of water and 20 ml. of H_2SO_4 (sp.gr. 1.84). (Add the acid in small doses.) When decomposition is complete, filter and wash with hot water. Discard the residue. Evaporate the filtrate to a volume of about 75 ml. and proceed as in "A" for the electrolytic separation of aluminum and zinc.

After separating most if not all of the zinc, transfer the electrolyte and washings to a 600-ml. beaker, add about 5 g. of tartaric acid (in solution), 5 g. of NH_4Cl and 10 ml. of a saturated solution of microcosmic salt. Make the solution alkaline with NH_4OH (sp.gr. 0.9) adding sufficient NH_4OH to have present 15 ml. for every 100 ml. of solution. Stir vigorously and allow to stand over night. Filter and wash with cold dilute NH_4OH (1 : 9), ignite and weigh as $Mg_2P_2O_7$. Multiply by 0.2184 for Mg. Run in duplicate.

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NOTE.—Should the solution after standing over night appear clear or should transparent crystals form, the magnesium has not been completely precipitated. A vigorous stirring at this point should completely precipitate the magnesium. Allow to stand several hours or preferably over night and proceed as outlined above.

C. DETERMINATION OF CADMIUM AND IRON

Weigh 30 g. of the sample into a 600-ml. beaker, add 100 ml. of water and 34 ml. of H_2SO_4 (sp.gr. 1.84). (Add the acid in small doses.) When decomposition is complete, add 10 g. of Na_2SO_4, dilute to a volume of 350 ml. with water, warm and pass H_2S for 30 minutes. Allow to stand in a warm place for 2 hours and again pass H_2S. Filter and wash. Reserve the filtrate (Filtrate No. 1).

Throw the paper containing the precipitate back into the original beaker, add 10 ml. of HNO_3 (sp.gr. 1.42) and 10 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of SO_3. Clear up any discoloration due to carbonizing of the paper by adding a few drops of HNO_3 (sp.gr. 1.42) to the hot solution. Cool, add 5 ml. of water, bring to boiling, cool, allow to stand an hour or so, filter and wash with cold H_2SO_4 (1 : 9). Discard the residue.

To the filtrate add 5 ml. of HNO_3 (sp.gr. 1.42), dilute to a volume of 150 ml with water and electrolyze for the removal of copper as described in "A." Remove and wash the electrodes, combine electrolyte and washings in a 600-ml. beaker and evaporate to fumes of SO_3. Cool, add 7 g. of Na_2SO_4, dilute to a volume of 300 ml. with water, warm and pass H_2S as before. Allow to stand as before. Again pass H_2S for 30 minutes, filter and wash with H_2S water. Reserve the filtrate (Filtrate No. 2).

Dissolve the precipitate by pouring 10 ml. of hot HNO_3 (1 : 1) through the paper, wash with hot water, add 5 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to strong fumes of SO_3. Cool, add a few ml. of water and again evaporate to fumes. Repeat the treatment with water and subsequent fuming to remove the last traces of nitric acid. Finally cool, take up with 50 ml. of water, bring to boiling, cool, neutralize with NH_4OH (1 : 2) and then make acid with H_2SO_4 (1 : 9) having 3 ml. in excess. Dilute to a volume of 100 ml. with water and electrolyze over night using a current of 0.5 amperes. Remove the cathode, rinse in water and then in 95% alcohol, dry at 110° C. for 10 minutes, cool and weigh as Cd. Run in duplicate.

Combine the reserved filtrates No. 1 and No. 2, boil to expel H_2S, oxidize the iron present by adding 10 ml. of H_2O_2 to the boiling solution, continue boiling to expel H_2O_2, cool and add a slight excess of a saturated solution of $KMnO_4$ to insure removal of the H_2O_2. Pass through a Jones reductor and titrate with N/20 $KMnO_4$ solution for iron. Run a blank through the reductor and correct for same. Run in duplicate.

NOTE.—Weigh out small pieces of metal. Sawings, drillings or filings are likely to be contaminated with iron from the tool used to take the sample.

D. DETERMINATION OF LEAD AND TIN

Solutions Required. *Lead Acid.*—See "Determination of Lead as Sulfate, Analysis of Manganese Bronze."

Ferric Chloride Solution.—Dissolve 25 g. of $FeCl_3 \cdot 6H_2O$ in 100 ml. of water and 10 ml. of HCl (sp.gr. 1.18); dilute to 500 ml. with water and mix.

Method.—Weigh 75–100 g. of sample into a 400-ml. lipless beaker, add 100 ml. of water and sufficient HNO_3 (sp.gr. 1.42) to affect solution. Avoid having a large excess of acid. Add the acid in 10 ml. doses allowing acid present to react with the alloy until it is almost spent before adding a subsequent dose. Heating the solution after the first violent reaction subsides accelerates solution of the alloy and hastens neutralization of the acid. If the above procedure is carried out properly complete solution of the alloy may be attained without having more than 10–15 ml. of free acid present. Finally cool, add 20 ml. of HNO_3 (sp.gr. 1.42), dilute to a volume of 300 ml. with water and electrolyze over night with a current of 1.0 ampere using a spiral anode and a cylindrical cathode. (See " Method A.") Transfer the cathode to a clean beaker and hold in reserve. Rinse the anode in water and then in 95% ethyl alcohol, dry at 110° C. for 10 minutes, cool and weigh as PbO_2. Multiply by 0.8643 for lead. (Reserve the water washings.) (To insure complete precipitation of the lead combine electrolyte and washings, add 10–15 ml. of HNO_3 (sp. gr. 1.42 and again electrolyze.) Dissolve the deposit of PbO_2 into a 200-ml. lipless beaker, with 10 ml. of HNO_3 (sp.gr. 1.42) and a few ml. of H_2O_2, add 50 ml. of lead acid and evaporate to fumes of SO_3. Cool, dilute to a volume of 50 ml. with water, bring to boiling, cool and allow to stand several hours. Filter and wash with lead acid. Dissolve the $PbSO_4$ with about 30 ml. of hot ammonium acetate solution containing 2 ml. of free acetic acid for each 100 ml. of solution, dilute to a volume of 150 ml., bring to boiling and add 5 ml. of a saturated solution of $K_2Cr_2O_7$. Allow to stand in a warm place several hours, filter on a prepared Gooch crucible, wash with hot water and finally with 95% ethyl alcohol. Dry at 105° C. for one hour, cool and weigh as $PbCrO_4$. Multiply by 0.6375 for lead. Run in duplicate.

After removing the lead, combine electrolyte and washings. Filter and wash with a hot solution of HNO_3 (1 : 49). Reserve the residue (Residue No. 1). Neutralize the filtrate with NH_4OH (sp.gr. 0.9) and make acid with HCl (sp.gr. 1.18) having 5 ml. of free HCl for every 100 ml. of volume. Cool and pass H_2S. Filter and wash with dilute HCl (1 : 49) through which H_2S has been passed. Discard the filtrate. If an appreciable amount of zinc has been precipitated as a sulfide throw the paper (and precipitate) back into the original beaker, add 10 ml. of HNO_3 (sp.gr. 1.42) and 10 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes. Destroy organic matter by adding HNO_3 (sp.gr. 1.42) to the hot solution. Cool, add 100 ml. of water, bring to boiling to dissolve salts, neutralize with NH_4OH, acidify with HCl as above and make a second precipitation with H_2S. Filter and wash. Reserve the residue (Residue No. 2).

Dissolve the deposit of copper from the cathode held in reserve with the least quantity of HNO_3 (sp.gr. 1.42), transfer to a 600-ml. beaker, add 10 ml. of ferric chloride solution, make slightly alkaline with NH_4OH (sp.gr. 0.9), dilute to a volume of 300 ml. with water, bring to boiling and allow to stand a half hour or so in a warm place. Filter and wash with hot water. If the precipitate retains copper, dissolve the $Fe(OH)_3$ into the beaker the filtration was made from with 20 ml. of hot HCl (1 : 1); wash with hot water. Make a second separation of iron with NH_4OH and filter through the same paper.

Should the precipitate still hold copper, make a third separation. When finally the precipitate of $Fe(OH)_3$ is freed of copper, transfer it, together with the two residues held in reserve, to a 300-ml. cone flask, add 10 ml. of HNO_3 (sp.gr. 1.42) and 20 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes. Destroy any organic discoloration with HNO_3 (sp.gr. 1.42). When the solution shows no discoloration even upon strong fuming cool, add a few ml. of water and fume again. Repeat with the addition of water and subsequent fuming two or three times to rid the solution of the last traces of nitric acid. Finally cool, add 100 ml. of water and 20 ml. of HCl (sp.gr. 1.18), reduce with iron, and proceed as described in " Determination of Tin in Battery Plate Metal." Titrate with approximately N/20 $KMnO_4$ solution. Carry along a blank and correct for same. Run in duplicate.

NOTE.—In general, the PbO_2 results come high. Report the lead figure obtained by the gravimetric method.

E. DETERMINATION OF MANGANESE

Solutions Required.—See " Determination of Manganese by the Persulfate Method, Analysis of Manganese Bronze."

Method.—Weigh 10 g. of the drillings into a 400-ml. beaker, add 80 ml. of the " solution for dissolving " and warm until completely in solution. Transfer to a 125-ml. graduated flask, cool to room temperature, make up to the mark with water, mix thoroughly and measure off 50 ml. of the solution into a 300-ml. Erlenmeyer flask. Boil until the oxides of nitrogen are expelled, dilute to 100 ml. with boiling hot water, add 20 ml. of $AgNO_3$ solution and 30 ml. of $(NH_4)_2S_2O_8$ solution and let stand over a hole on the steam bath until a full permanganate color has developed. Cool to below 25° C. and immediately titrate with standard arsenite solution to the disappearance of the pink color. Run in duplicate.

NOTES.—1. One g. of the metal requires 2.75 ml. of the "solution for dissolving" for solution.

2. Should the aliquoted portion contain more than 0.0015 g. of Mn, a precipitate of hydrated MnO_2 will form. In that case, measure off a smaller portion, add sufficient "acid mixture" to bring the acid mixture content up to 24 ml. and proceed as described above.

3. If the solution is allowed to stand too long a time, the color will fade. Warming for 15 minutes should convert all the Mn to permanganic acid.

4. Owing to the rigid specifications called for in this class of alloys and the tediousness of chemical analysis for impurities, especially tin, spectrographic methods are preferable. See "Tentative Method of Test for Quantitative Spectrochemical Analysis of Zinc Alloy Die Castings for Minor Constituents and Impurities," 1935 Book of A. S. T. M. Tentative Standards, p. 1488.

FUSIBLE METALS

Fusible metals are mixtures of lead and tin to which has been added bismuth, cadmium or both to lower the melting point. They may contain in addition small amounts of impurities, such as copper, arsenic, antimony, iron and zinc.

ANALYSIS OF WOOD'S ALLOY [23]

(ALLOY OF LEAD, TIN, BISMUTH AND CADMIUM)

Determination of Lead

Method.—Proceed exactly as in " Determination of Lead, Alloy of Lead, Copper, Antimony and Tin," General Methods.

Determination of Tin

Method.—Weigh 1 g. of the sawings into a 300-ml. cone flask, add 20 ml. of H_2SO_4 (sp.gr. 1.84) and heat on a hot plate until completely decomposed. Cool, add 100 ml. of cold water and 20 ml. of HCl (sp.gr. 1.2), reduce with iron and proceed as described in " Determination of Tin in Battery Plate Metal."

Determination of Bismuth

Reagents Required. ***Fusion Mixture.***—Weigh 100 g. of Na_2CO_3, 140 g. of K_2CO_3 and 100 g. of sulfur into a large porcelain mortar. Grind and mix thoroughly, transfer to a glass-stoppered bottle and reserve for use.

KSH Wash Solution.—See " Determination of Lead, Bismuth, etc. in Tin Base Bearing Metal."

Method.—Weigh 1 g. of the sawings into a 250-ml. beaker, add about 10 ml. of water, heat, and add sufficient HNO_3 (sp.gr. 1.42), a little at a time, until the alloy is decomposed. Evaporate to dryness, digest with 10 ml. of HNO_3 (sp.gr. 1.42), dilute to 50 ml. with water, bring to boiling and allow to stand, and settle for one hour keeping the temperature just below the boiling point. Filter, keeping the solution hot, through a small close-textured paper to which a little paper pulp has been added and wash with hot dilute HNO_3 (1 : 49). Reserve the filtrate.

Transfer the paper and precipitate to a small porcelain crucible, dry and ignite. Mix the residue with 4 g. of fusion mixture, cover with 4 g. of the fusion mixture and heat until in quiet fusion; heat 20 minutes longer. Cool, leach with as little water as possible, remove and wash the crucible. Combine washings with the main solution. The supernatant solution should be of a clear yellow color. Filter and wash with warm (not hot) KSH wash solution. (The filtrate may be used for the determination of antimony. See " Determination of Antimony.")

Dissolve the residue with 15 ml. of hot HNO_3 (1 : 2), wash with hot water, boil to a volume of 25 ml. and allow to stand for one hour keeping the temperature just below the boiling point. If an insoluble residue is present, filter on a small close-textured paper to which a little paper pulp has been added and

[23] Methods of National Lead Company Research Laboratories.

wash with hot dilute HNO_3 (1 : 49). Discard the residue. Combine the filtrate with the original filtrate from the H_2SnO_3 separation.

Boil the combined filtrates down to a volume of 100 ml., make just neutral with NH_4OH (1 : 3) as shown by a piece of litmus paper and then add 5 ml. of HCl (1 : 9) in excess. Dilute to a volume of 400 ml. with boiling hot water and allow to stand in a warm place for several hours. Filter and wash with hot water. Reserve the filtrate.

Dissolve the precipitate from the filter with hot HCl (1 : 1) and wash alternately, first with hot water and then with hot HCl (1 : 1). Evaporate the solution down to a volume of about 1 ml., dilute to a volume of 400 ml. with boiling hot water and allow to stand as before. Filter on a weighed porcelain Gooch crucible and wash with hot water. Transfer the filtrate to a clean beaker and reserve. Finally wash the precipitate on the Gooch once or twice with 95% alcohol, dry at 110° C. for 30 minutes, cool and weigh as BiOCl. Multiply by 0.8024 for bismuth.

Notes.—1. During the solution of the alloy, lead nitrate may separate out and precipitated H_2SnO_3 may coat undissolved alloy and prevent further solution. In such a case, dilute with sufficient hot water to dissolve lead nitrate and detach the H_2SnO_3 coating from undissolved alloy with a glass rod.

2. The fusion of the H_2SnO_3 is best conducted by placing the small porcelain crucible inside a larger one. Cover both crucibles. Set the covers on the crucibles in an inverted position, first breaking off the small ring handles of the covers before placing them on the crucibles.

3. Start the fusion at a low heat and gradually bring the temperature up. If started at too high a temperature the melt will froth over the top.

4. If the melt is leached with an excessive amount of water, the sulfides, especially iron sulfide, will not separate but will remain in solution in a colloidal state. In such a case, evaporate to a volume of about 50 ml., add about 20 ml. of KSH stock solution, stir, and allow to stand in a warm (not hot) place until the supernatant solution is of a clear yellow color. The addition of a few grams of NH_4Cl accompanied with vigorous stirring will accelerate the precipitation of the colloidal sulfides. (Do not boil.)

Determination of Cadmium and Copper

Electrodes.—See " Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

Method.—Combine the two filtrates from the BiOCl separations, evaporate to a volume of about 40 ml., add 10 ml. of H_2SO_4 (1 : 1), bring to boiling, cool, allow to stand 30 minutes or so, filter and wash with cold water. Discard the residue. Dilute the filtrate to a volume of 300 ml., warm and pass H_2S for 30 minutes, allow to stand in a warm place an hour or so and again pass H_2S for 15 minutes. Filter and wash two or three times with H_2S water containing a little $(NH_4)_2SO_4$. Throw the paper containing the precipitate back into the beaker the filtration was made from, add 10 ml. of HNO_3 (sp.gr. 1.42) and 5 ml. of H_2SO_4 and evaporate to fumes, taking the necessary steps to remove carbonaceous matter. (See " Determination of Lead, Bismuth, etc. in Tin Base Bearing Metal.") Cool, take up with a few ml. of water and fume. Again cool, take up with water and fume. Finally cool, dilute to a volume of 40 ml., bring to boiling, cool, allow to stand at least two hours, filter and wash with cold dilute H_2SO_4 (1 : 9). Discard the residue. Neutralize the filtrate with NH_4OH (1 : 2) and then make acid with 3 ml. of H_2SO_4 (1 : 9) in excess, dilute to a volume of 150 ml. and electrolyze over night with a

current of 1.0 ampere, using a platinum spiral for anode and a platinum cylinder for cathode. Remove the cathode, rinse in water and in 95% alcohol, dry at 110° C. for 10 minutes, cool and weigh as cadmium plus copper.

Dissolve the deposit from the cylinder with 5 ml. of HNO_3 (sp.gr. 1.42) and wash the electrode free from cadmium with water. Combine the electrolyte and washings and evaporate to a small volume. Wash into a small porcelain crucible and evaporate to dryness. Take up with 1 ml. of HNO_3 (1 : 1) and proceed as in " Determination of Copper in Solder."

Having determined the amount of copper present deduct from the weight of copper plus cadmium. The difference is cadmium.

NOTE.—Do not lose any of the electrolyte in removing the cathode.

Determination of Antimony

(a) **General Method.**—Dissolve 5 g. of the sawings in dilute HNO_3 and proceed as in " Determination of Bismuth " up to the point where the H_2SnO_3 precipitate after fusion and leaching, has been filtered and washed.

Warm the alkaline sulfide filtrate, add $KClO_3$, a little at a time, and HCl (sp.gr. 1.18) until the solution is strongly acid and the sulfur has been oxidized. The solution should be clear and distinctly yellow. Dilute to a volume of 300 ml. with water and boil down to a volume of 200 ml. When the chlorine has been expelled, add 10 ml. of copper solution (2.0 g. of $CuSO_4 \cdot 5H_2O$ dissolved in 500 ml. of water), make slightly alkaline with NH_4OH (sp.gr. 0.9), then just acid with a saturated solution of $H_2C_2O_4$, add 12 g. of solid $H_2C_2O_4$, dilute to a volume of 400 ml. and proceed as in " Determination of Antimony, Analysis of Alloys of Lead, Copper, Antimony and Tin," General Methods.

NOTE.—Care must be exercised in rendering the alkaline sulfide solution acid with HCl. If the acid is not added in small doses, especially when the solution is hot, the rapid evolution of H_2S will make the solution froth over the top of the beaker.

(b) **Rapid Method.**—Dissolve 5 g. of the sawings in dilute HNO_3 and proceed as in " Determination of Bismuth " up to the point where the H_2SnO_3 has been filtered and washed.

Transfer the paper containing the H_2SnO_3 and $HSbO_3$ to a 350-ml. Erlenmeyer flask and proceed as in " Determination of Antimony, Analysis of Bronze Bearing Metal."

Determinatin of Iron

Proceed as in " Determination of Iron, Determination of Lead, Bismuth, etc. in Tin Base Bearing Metal."

Determination of Zinc

Proceed as in " Determination of Zinc in Solder."

Determination of Arsenic

Proceed as in " Determination of Arsenic, Analysis of Alloys of Lead, Tin, Antimony and Copper," General Methods.

SILVER ALLOYS

ANALYSIS OF SILVER SOLDERS [24]

(ALLOY OF SILVER, COPPER, CADMIUM AND ZINC) [25]

Determination of Silver

Solutions Required. *Dilute Hydrochloric Acid Solution.*—To 3 ml. of HCl (sp.gr. 1.18) add 97 ml. of water. One milliliter of this solution should precipitate about 0.038 g. of silver.

Method.—Weigh 1 g. of the sawings into a 250-ml. beaker, add 20 ml. of HNO_3 (1 : 4), gently warm until solution is complete and, then boil to expel the oxides of nitrogen. Dilute to a volume of 175 ml., heat to boiling and add, drop by drop with constant stirring, sufficient dilute HCl solution to precipitate all the silver present. Avoid a large excess of the precipitant. Cool in a dark place. When the solution is cold and the precipitate has settled, test the clear solution with a drop of the dilute HCl solution to determine whether or not the precipitation is complete. Filter on a weighed porcelain Gooch crucible, and wash with cold dilute HNO_3 (1 : 200); finally wash once with cold water. Reserve the filtrate.

Place the Gooch crucible inside a porcelain crucible, dry and heat until the material begins to show signs of fusion. Cool and weigh as AgCl. Multiply by 0.7526 for Silver.

Notes.—1. If tin is present, as shown by a precipitate of metastannic acid when dissolving in nitric acid, it should be filtered off as in "Determination of Tin," before proceeding with the determination of silver. (See note under " Determination of Tin.")

2. If it is desired to determine the silver by a combination assay method, dissolve an amount of sample which will contain about 0.3 g. of silver in dilute HNO_3 (1 : 4), precipitate the silver as AgCl, filter and wash and proceed as in "Assay of Copper Bullion" in chapter under Fire Assay for Gold and Silver.

Determination of Copper

Method.—Transfer the filtrate from the AgCl separation to a 400-ml. beaker, add 5 ml. of H_2SO_4 (sp.gr. 1.84), evaporate to fumes of H_2SO_4, cool,

[24] The methods given under "Analysis of Silver Solders" are A. S. T. M. methods, excepting those for cadmium and zinc. See A. S. T. M. Methods of Chemical Analysis of Metals, p. 193, December, 1936.

[25] See Specifications of Silver Solders" 1936 Book of A. S. T. M. Standards, Part I, p. 691.

dilute with 50 ml. of water, bring to boiling, transfer to a 200-ml. lipless beaker, add 3 ml. of HNO_3 (sp.gr. 1.42), cool, dilute to 150 ml. with water and proceed as in " Determination of Copper, Analysis of Manganese Bronze."

Determination of Cadmium

Method.—Transfer the electrolyte and washings to a 600-ml. beaker, evaporate to fumes of H_2SO_4, cool, add 7 g. of $(NH_4)_2SO_4$, dilute to a volume of 300 ml., bring to boiling and make two separations of the cadmium from zinc with H_2S. Dissolve the final precipitate with 10 ml. of HNO_3 (1 : 1), add 5 ml. of H_2SO_4 and evaporate to fumes of SO_3. Proceed as outlined in " Determination of Cadmium and Iron, Analysis of Zinc Base Die Casting Alloy."

Determination of Zinc [26]

Solutions Required. ***Standard Potassium Ferrocyanide Solution.***—Dissolve 21.7 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ in water, filter, dilute to 1000 ml. with water and mix. Standardize by weighing out 0.2 to 0.25 g. of pure zinc into a 400-ml. beaker, dissolve with 7 ml. of HCl (sp.gr. 1.18), dilute to 200 ml., add about 7 g. of NH_4Cl and titrate as in the " Determination of Zinc " in the sample. Deduct 0.2 ml. from the burette reading as a correction for end-point. Each milliliter should approximately equal 0.005 g. of zinc.

Uranyl Nitrate Indicator.—Dissolve 5 g. of $UO_2(NO_3)_2 \cdot 3H_2O$ in 100 ml. of water.

Method.[27]—Combine the two reserved filtrates from the cadmium sulfide separations with the electrolyte and washings, boil to expel dissolved gas, add 5 ml. of HNO_3 (sp.gr. 1.42) and evaporate to a volume of about 300 ml. Make slightly alkaline with NH_4OH (sp.gr. 0.9), allow to stand for any iron present to settle out, filter and wash first with dilute NH_4OH (1 : 4) and then with hot water. Dissolve the precipitate with a little hot HCl (1 : 1) and make a second separation of iron with NH_4OH. Combine the two filtrates from the iron separations, neutralize with HCl (sp.gr. 1.18), make slightly alkaline with NH_4OH (sp.gr. 0.9), and pass H_2S for 15 minutes. While the H_2S is passing, make slightly acid with 80% acetic acid and continue passing H_2S for 15 minutes longer. Filter on a close-textured paper to which a little paper pulp has been added and wash two or three times with H_2S water to which a little acetic acid has been added. Transfer the paper containing the precipitate to the beaker the filtration was made from, add 20 ml. of HCl (1 : 2), open up the filter so that the precipitate will come in contact with the acid, and allow to stand in a warm place until the ZnS has completely dissolved. Dilute to a volume of 200 ml. with water, add about 7 g. of NH_4Cl, pass H_2S for five minutes, heat to 80° C. and titrate with the standard $K_4Fe(CN)_6$ solution until a drop of the solution added to a drop of the indicator on a spot plate gives a slight tinge of brown. Deduct 0.2 ml. and calculate to per cent of zinc.

[26] See "Rapid Ferrocyanide Method for Determining Zinc in Ores" in chapter under Zinc.

[27] For the titration with ferrocyanide solution using an inside indicator see "Titration in Acid Solution—Separating of Zinc as Sulfide" in chapter under Zinc.

NOTES.—1. If the sample contains more than 25% of zinc, take such an aliquot portion as will not contain more than 0.25 g. It is advisable to aliquot before separating the zinc as a sulfide.

2. If nickel and manganese are present separate the zinc as a sulfide in a formic acid solution see "Determination of Zinc, Analysis of Bronze Bearing Metal."

DETERMINATION OF TIN

Method.—Dissolve a separate 5 g. sample with 100 ml. of HNO_3 (1 : 4), boil to expel the oxides of nitrogen, dilute to a volume of 250 ml., bring to boiling and allow to stand for about one hour keeping the temperature just below the boiling point. Filter on double 7 cm. ashless papers, being careful to keep the solution hot during the filtration and wash with hot water. Reserve the filtrate for the determination of lead. Transfer the paper and precipitate to a weighed porcelain crucible, dry, ignite, cool and weigh as SnO_2. Multiply by 0.7877 for Tin.

NOTE.—Every precaution must be taken to avoid contamination by chlorides in order to prevent the precipitation of AgCl during the determination of tin.

DETERMINATION OF LEAD

Solutions Required.—See " Determination of Lead as Sulfate, Analysis of Manganese Bronze."

Method.—Heat the filtrate from the H_2SnO_3 separation to boiling and precipitate the silver as in " Determination of Silver." Filter on a closely-woven paper and wash with cold dilute HNO_3 (1 : 200). Add 80 ml. of lead acid and evaporate to fumes of H_2SO_4. To insure complete removal of chlorides, cool, add a few ml. of water and fume again. Cool, add 70 ml. of water, heat to boiling and proceed as in " Determination of Lead as Sulfate, Analysis of Manganese Bronze."

Transfer the filtrate from the $PbSO_4$ separation to a clean beaker before the final washing with alcohol and reserve for the determination of iron.

NOTE.—In order to avoid "spitting" during the evaporation with lead acid it is suggested to heat over a burner holding the beaker with a pair of tongs and twirling as the evaporation is carried on.

DETERMINATION OF IRON

Solutions Required.—See " Determination of Iron, Analysis of Manganese Bronze."

Method.—To the filtrate from the $PbSO_4$ separation add 3 ml. of HNO_3 (sp.gr. 1.42) and remove copper by electrolysis. Remove the electrodes, wash them with water, transfer the electrolyte and washings to a 600-ml. beaker, boil to expel dissolved gases and add 5 ml. of HNO_3 (sp.gr. 1.42). Cool, add 5 g. of NH_4Cl and sufficient NH_4OH (sp.gr. 0.9) to make the solution alkaline and to hold up the zinc, bring to boiling and allow to stand in a warm place an hour or so. Filter and wash with hot water. Dissolve the precipitate through the filter paper with hot dilute HCl (1 : 1) and make a second separation of iron with NH_4OH. Combine the two filtrates and reserve for the determination of nickel. Dissolve the final precipitate through the paper with 100 ml. of dilute H_2SO_4 for reductor, add a few drops of a strong solution of $KMnO_4$ until

a distinct color persists, bring to boiling, pass through the reductor and proceed as in " Determination of Iron, Analysis of Manganese Bronze."

Determination of Nickel

Solutions Required: ***Dimethylglyoxime Solution.***—Dissolve 5 g. of dimethylglyoxime in 500 ml. of grain alcohol and filter before using.

Method.—Evaporate the combined filtrates from the $Fe(OH)_3$ separations to a volume of about 100 ml., make barely acid with HCl (sp. gr. 1.18), heat to boiling, add 5 ml. of dimethylglyoxime solution for each 0.1 g. or fraction of nickel present and proceed as in " Determination of Nickel, Analysis of Bronze Bearing Metal."

HEAT RESISTING ALLOYS

ANALYSIS OF NICHROME [28]

(ALLOY OF NICKEL, CHROMIUM, IRON AND MANGANESE)

Determination of Nickel

Electrodes.—See " Determination of Copper, Analysis of Manganese Bronze."

Solutions Required. ***Nitro-Hydrochloric Acid.***—Mix 10 ml. of HNO_3 (sp.gr. 1.42), 30 ml. of HCl (sp.gr. 1.18) and 40 ml. of water.

Dilute Acetic Acid.—Mix 1 ml. of acetic acid (sp.gr. 1.04) and 3 ml. of water.

Potassium Thiocarbonate.—Saturate 125 ml. of a 5% solution of KOH with H_2S, add 125 ml. of KOH solution (5%) and 10 ml. of CS_2 and heat moderately. Decant the dark red liquid from undissolved CS_2 and preserve in a well closed flask.

Sodium Dimethylglyoxime.—Dissolve 3 g. of dimethylglyoxime in 100 ml. of NaOH (3%), made fresh each time used.

Method.—Weigh 1 g. of the alloy into a 600-ml., beaker dissolve in 20 ml. of nitro-hydrochloric acid, add 20 ml. of H_2SO_4 (1 : 1) and evaporate to fumes of H_2SO_4. Cool, add 100 ml. of water and allow the solution to digest at a low heat until all salts have dissolved. Filter on a small paper and wash with hot water. If an insoluble residue is present wash with dilute H_2SO_4 (1 : 99). Transfer the residue to a platinum crucible, dry, ignite at a low heat, add 2 ml. of HF and 2 drops of H_2SO_4 (sp.gr. 1.84), evaporate to dryness, heat over a low flame to expel free H_2SO_4, cool and fuse with a little Na_2CO_3. Dissolve the melt in HCl, and add to the main nickel solution.

Transfer the nickel solution to a 250-ml. graduated flask, make up to the mark with water at room temperature and mix. Draw off exactly 50 ml. into

[28] A. S. T. M. Methods of Chemical Analysis of Metals, p. 203, Dec. 1936.

a 600-ml. beaker, add 25 ml. of a 20% solution of tartaric acid (enough to hold all the iron and chromium in solution), make alkaline with NH_4OH and then make acid with 15 ml. of HCl (sp.gr. 1.18) in excess. Add 20 to 30 ml. of the sodium dimethylglyoxime solution, neutralize with NH_4OH and then make just acid with the dilute acetic acid. Stir the solution vigorously and allow to stand at a temperature of from 75 to 90° C., with occasional stirring, for 30 minutes. Filter on a weighed Gooch crucible, wash with hot water, dry at 110° C. to constant weight, cool and weigh as nickel dimethylglyoxime. Multiply by 0.2032 for nickel.

If greater accuracy is desired, use a larger aliquot portion with proportionally larger amounts of reagents and filter the nickel dimethylglyoxime precipitate on a 15 cm. paper and wash 18 or 20 times with hot water. Dissolve the precipitate off the paper with boiling dilute HNO_3 (1 : 3) and wash the filter thoroughly with hot water. Add 10 ml. of dilute H_2SO_4 (1 : 1) and boil the liquid gently until strong fumes of SO_3 are evolved. Cool, add 10 ml. of HNO_3 (sp.gr. 1.42) and repeat the evaporation. Rinse the cover and sides of beaker with a fine jet of water and fume the solution again to insure the expulsion of every trace of HNO_3. Cool, add approximately 50 ml. of cold water and boil the contents of the beaker for several minutes, which should result in a perfectly clear solution.

Make the solution alkaline with 25 ml. of NH_4OH (sp.gr. 0.9) in excess, insert electrodes, and electrolyze with a current of from 1 to 2 amperes until the solution has become colorless. Continue the electrolysis for at least 15 minutes longer, and then test the solution by adding 1 or 2 drops of it to a solution of potassium thiocarbonate. A pink color indicates the presence of nickel. Remove the cathode quickly, rinse it in water and then in absolute alcohol, dry for a few minutes at a temperature of 80 to 100° C., cool and weigh as metallic nickel.

Note.—If an alcoholic solution of dimethylglyoxime was used to precipitate the nickel, the contents of the beaker should be digested at a temperature just short of the boiling point until the odor of alcohol can no longer be detected before filtering.

Determination of Chromium

Solutions Required. ***Ferrous Ammonium Sulfate Solution.***—Dissolve 39.25 g. of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in water, add 20 ml. of H_2SO_4 (1 : 1), dilute to 1000 ml. and mix.

Standard Potassium Permanganate Solution (0.1 N).—For its preparation and standardization against $Na_2C_2O_4$ see " Potassium Permanganate, Standard Solutions " in chapter under Reagents. Each milliliter should equal 0.001734 g. of chromium.

Method.—Treat 1 g. of the sample in a covered 600-ml. beaker with 10 ml. of perchloric acid (60%). Heat to strong fumes of perchloric acid to aid in the solution of the alloy, and continue the heating for 3 or 4 minutes after the alloy has dissolved completely to insure oxidation of the larger part of the chromium to the sexivalent state. Add 100 ml. of hot water and heat to boiling for several minutes to expel chlorine. Remove from the plate and add 20 ml. of dilute H_2SO_4 (1 : 1) and 5 ml. of HNO_3 (sp.gr. 1.42). Dilute to 250 ml. with hot water, add 10 ml. of $AgNO_3$ (0.5%), 3 g. of ammonium persulfate and 5 or 6

drops of $KMnO_4$ solution (2.5%). Boil for 5 minutes or longer, add 20 ml. of NaCl solution (10%) and boil for 10 minutes after the permanganic acid or any MnO_2 formed has dissolved completely, in order to make sure that all chlorine has been expelled. Cool to room temperature and dilute with cold water to 400 ml. Treat with 2 ml. of H_3PO_4 (sp.gr. 1.72), add from a burette ferrous ammonium sulfate solution until the solution turns green and then add 5 ml. in excess. Titrate this excess back with 0.1 N potassium permanganate.

In a clean flask, place 50 ml. of the ferrous ammonium sulfate, add 10 ml. of H_2SO_4 (1 : 1) and titrate with the standard $KMnO_4$ solution. From this titration calculate the number of ml. of $KMnO_4$ solution necessary to titrate the amount of ferrous ammonium sulfate solution added to the sample. The difference between the number of ml. of $KMnO_4$ solution calculated and the number used for the titration of the sample represents the chromium present and the percentage is found by multiplying this volume by 100 times the chromium titre of the $KMnO_4$ solution.

NOTE.—The strength of the ferrous ammonium sulfate may change from day to day. Its strength in terms of $KMnO_4$ solution should be ascertained each time the determination is made.

DETERMINATION OF IRON

Solutions Required. ***Stannous Chloride Solution.***—Dissolve 50 g. of $SnCl_2 \cdot 2H_2O$ in 100 ml. of HCl (sp.gr. 1.18) and dilute to 1000 ml.

Standard Potassium Permanganate Solution.—See " Determination of Chromium." Each milliliter equals 0.005584 g. of iron.

Method.—For alloys containing 10% or more of iron, use a 1 g. sample, and for alloys containing 2% or less of iron, use a 3 g. sample. Treat the sample in a 500-ml. Erlenmeyer flask fitted with a Meyer bulb or trap with 20 to 50 ml. of perchloric acid (60%) at a temperature of 203° C. or higher until the alloy has dissolved completely, and continue the boiling of the acid for five minutes longer to aid in the complete oxidation of the chromium to the sexivalent state. The tall flask and bulb (or trap) are used to prevent the loss of $FeCl_3$ by volatilization, which happens if a covered beaker is used. Add approximately 200 ml. of hot water, an excess of about 10 ml. of NH_4OH (sp.gr. 0.9) and 5 g. of ammonium persulfate. Boil for 5 minutes, filter and wash thoroughly with hot water. Dissolve the $Fe(OH)_3$ in hot HCl (1 : 4) and repeat the precipitation with NH_4OH and ammonium persulfate, and the filtration. Dissolve the $Fe(OH)_3$ in the least possible amount (15 to 25 ml.) of boiling, dilute HCl (1 : 4) and wash the filtrate thoroughly with water. Heat to boiling, add stannous chloride solution slowly and with stirring to discharge the yellow color of the ferric chloride and to provide a few drops in excess. Finish the determination by the Zimmerman-Reinhardt method.[29]

DETERMINATION OF MANGANESE

Solutions Required.—See " Determination of Chromium."

Method.—Decompose 1 g. of the sample with 20 ml. of perchloric acid (60%) exactly as outlined in the determination of chromium. Add 200 ml. of

[29] Blair, A. A., "The Chemical Analysis of Iron," 8th Ed., p. 248.

warm water, an excess of about 10 ml. of NH_4OH (sp.gr. 0.9) and 5 g. of ammonium persulfate. Boil for 5 minutes, filter on two superimposed 11 cm. filter papers, supported on a Büchner funnel, gentle suction being employed. Wash the precipitate thoroughly with hot water. Dissolve the precipitate of $Fe(OH)_3$ and MnO_2 in 75 ml. of hot HNO_3 (sp.gr. 1.135) and a few drops of H_2SO_3. Wash the filter thoroughly with hot water. Repeat the precipitation with NH_4OH and ammonium persulfate, and the filtration. Dissolve the precipitate in 50 ml. of hot HNO_3 (sp.gr. 1.135) and a few drops of H_2SO_3, and wash the filter with HNO_3 of the same strength. Transfer to a 300-ml. Erlenmeyer flask and boil for several minutes to expel oxides of nitrogen. Treat cautiously with 0.5 g. of sodium bismuthate and heat to boiling for 1 or 2 minutes. Clear with a sufficient excess of H_2SO_3 and boil for 2 or 3 minutes longer. Cool to 15° C., add 1 to 2 g. of sodium bismuthate, shake vigorously for 1 minute, dilute with an equal volume of cold water and filter at once on an ignited asbestos or alundum filter. Wash with cold HNO_3 (3%). Add from a burette 20 to 25 ml. (depending on the amount of permanganic acid) of ferrous ammonium sulfate solution and titrate the excess with standard $KMnO_4$ solution.

To ascertain the amount of manganese present proceed exactly as in " Determination of Chromium."

Determination of Carbon

See " Determination of Carbon by the Direct Combustion Method, Standard Methods of Chemical Analysis of Plain Carbon Steel," in the chapter under Iron and Steel.

Determination of Insoluble Residue

Method.—Treat 5 g. of the sample (if low in insoluble residue 10 g. should be taken) with from 200 to 400 ml. of HCl (sp.gr. 1.18) at a temperature of from 60 to 70° C. until the reaction appears to be complete and then add 1 to 2 ml. of HNO_3 (sp.gr. 1.42). Boil for 2 minutes, dilute with an equal volume of hot water, filter and wash with hot dilute HCl (1 : 19).

Ignite the residue at a low heat in a platinum crucible, treat with HF and a few drops of H_2SO_4 (1 : 1), and evaporate just to fumes of H_2SO_4. If any residue remains, add 10 ml. of water, filter on a 9 cm. paper and wash with hot water. Ignite any residue remaining on the paper and weigh. Calculate to per cent of insoluble.

Accuracy.—In the case of an insoluble residue of 0.05%, duplicate determinations should check within $\pm 0.02\%$ insoluble residue.

Determination of Silicon

Method.—Treat a two to five factor weight sample (one factor weight equals 0.4672 g.) in a covered 300-ml. porcelain casserole with 15 to 35 ml. of perchloric acid (60%) at a temperature of 203° C. (the boiling point of the acid) until the alloy has dissolved completely, and continue boiling for 10 minutes longer. Add 100 ml. of warm water, boil for several minutes and filter on an 11 cm. paper of close texture. Wash six or eight times with hot water, once with H_2SO_3 (10%) to reduce any chromic acid held in the filter, and then thoroughly with hot water.

Transfer the paper and precipitate to a small platinum crucible, dry, and ignite, at first at a dull red heat and finally at 1050 to 1100° C. Cool and weigh. Add 2 drops of H_2SO_4 (1 : 1) and several ml. of HF and evaporate until all the H_2SO_4 has been expelled. Ignite the crucible again at 1050 to 1100° C., cool and weigh.

The difference between the first and second weights multiplied by 100 and divided by the weight of sample taken gives the percentage of silicon in the sample.

Determination of Sulfur

See "Determination of Sulfur by the Evolution-Titration Method, Standard Methods of Chemical Analysis of Plain Carbon Steel," in the chapter under Iron and Steel with the following modifications:

1. Due to the length of time (30 minutes) required for solution of the alloy, closer observation is necessary than in the analysis of steel.
2. During the solution of the sample, care must be exercised in order that absorbing solution is not drawn back into the flask.
3. There is danger of contamination from rubber hose connections and rubber stoppers.
4. The use of a gas flame is a possible source of sulfur contamination and an electric heater is recommended.

Accuracy.—In the case of a sulfur content of 0.05%, duplicate determinations should check within ±0.003%.

CORROSION RESISTING ALLOYS[30]

ANALYSIS OF STELLITE [31]

(ALLOY OF COBALT, CHROMIUM AND MOLYBDENUM) [32]

Electrodes.—See "Determination of Copper by the Electrolytic Method, Analysis of Manganese Bronze."

Determination of Cobalt

Method.—Dissolve 1 g. of the sample in 30 ml. of HCl (sp.gr. 1.18) and 30 ml. of HNO_3 (sp.gr. 1.42). Evaporate to a volume of 20 ml., add 100 ml. of HNO_3 (sp.gr. 1.42) and evaporate to dryness. Do not bake. Add 50 ml.

[30] See "Analysis of Stellite, Akrite and Similar Complex Alloys," Chem. Abs., 23, 5128 (1929).

[31] Johnson C. M., "Rapid Methods for the Chemical Analysis of Special Steels, Steel-Making Alloys, and Graphite," p. 322, John Wiley and Sons, N. Y., 1914.

[32] For methods of separation and estimation of W, Mo, U, V, Ti, Zr, As, P and Cr, see "Analytical Methods for Certain Metals," Department of the Interior, Bureau of Mines, Bull., 212, p. 18, 1923.

of HCl (sp.gr. 1.18), evaporate to a volume of 20 ml., transfer to a 1000-ml. wash bottle flask and dilute to 200 ml. with water. Add Na_2O_2, a gram at a time, until a black precipitate forms and tends to settle, and then add 10 g. more of Na_2O_2 and 10 g. of Na_2CO_3. Bring to boiling, continue to boil for 10 minutes, cool, filter on double 15 cm. papers and wash with water containing a little Na_2O_2. Dissolve the precipitate through the paper with 60 ml. of hot HCl (1 : 1) into the original flask and make a second separation of cobalt and iron with Na_2O_2 and Na_2CO_3. Repeat the peroxidations until the final filtrate is free of yellow color. Three peroxidations should suffice. Discard the filtrates. Finally dissolve the precipitate with 60 ml. of hot HCl (1 : 1) into the original flask and wash with hot water. Transfer the papers to a porcelain crucible, dry, ignite, cool, add 5 ml. of HCl (sp.gr. 1.18) to dissolve the remaining residue and add to the main cobalt and iron solution.

Transfer the combined solutions from the flask to a 600-ml. beaker and make a basic acetate separation of the iron. (See " Separation of Manganese from Iron and Aluminum, Basic Acetate Method " in chapter under Managnese.) Dissolve the precipitate with hot HCl (1 : 1) and make a second basic acetate separation. Combine the two filtrates and washings. Reserve the precipitate for the determination of iron.

Boil the combined filtrates from the basic acetate separations down to a volume of 500 ml., make just alkaline with NH_4OH (1 : 1), pass H_2S for about 20 minutes and then while the H_2S is passing, make slightly acid with acetic acid and continue passing H_2S for 15 minutes longer. Filter but do not wash the precipitate. Wash the precipitate from the paper back into the beaker, unfold the filter and place it on the cover glass with the side of the filter that came in contact with precipitate exposed to view. Place cover glass and filter on the beaker, add to the contents of the beaker 30 ml. of a mixture composed of equal parts of HNO_3 (sp.gr. 1.42) and HCl (sp.gr. 1.18) and heat on the hot plate until the acid fumes have dissolved from the filter any adhering CoS. Do not heat too long a time or the filter will disintegrate. Wash down the filter and cover glass. Discard the filter.

To the solution add 10 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of SO_3. Cool, add 2 ml. of water and bring to fumes a second time to remove the last traces of HNO_3 and HCl. Cool, add 100 ml. of water and boil to dissolve salts. Transfer the solution to a 600-ml. beaker, cool, make alkaline with 60 ml. of NH_4OH (sp.gr. 0.9) in excess, dilute to a volume of about 400 ml. and electrolyze over night with a current of 1.0 ampere. Remove the cathode; wash twice with water and once with 95% alcohol; dry at 110° C., cool and weigh as metallic cobalt.

Notes.—1. When manganese is present, a solution containing 30 ml. of water and 2 g. of Na_2O_2 is added to the alkaline solution just before plating out the cobalt.

2. If any nickel is present it will plate out along with the cobalt. In that case dissolve both metals from the cylinder with HNO_3 (sp.gr. 1.42) and determine the nickel by the glyoxime method. (See "Precipitation of Nickel by Dimethylglyoxime" in chapter under Nickel.) Deduct for nickel. The difference is cobalt.

3. Johnson folds a small square of cheese cloth in with the filter at the apex to prevent the alkaline solution from tearing the filter when filtering after a peroxidation.

Determination of Iron

Dissolve the precipitate obtained from the separation of the cobalt with hot HCl (1 : 1), add NH_4OH (sp.gr. 0.9) until a permanent precipitate forms, boil, allow to settle, filter and wash with dilute ammonia and hot water until all NH_4Cl is removed. Proceed as in " Determination of Iron, Analysis of Manganese Bronze."

Note.—Run a blank on chemicals used.

Determination of Chromium

Solutions Required. *Ferrous Ammonium Sulfate and Standard $KMnO_4$.* —See " Determination of Chromium, Analysis of Nichrome."

Method.—Fuse 0.5 g. of the sample with 8 g. of Na_2O_2 in a 35-ml. nickel crucible. Keep the fusion molten for 5 minutes. Cool, place the crucible on its side, in a 375-ml. porcelain casserole, cover with a watch glass and cautiously add sufficient cold water to cover about half the crucible. When the melt is completely dissolved, remove the crucible and wash it with hot water. Combine the solution and washings, filter and wash thoroughly with water containing a little Na_2O_2. Discard the residues if free from undecomposed alloy. (See " Sodium Peroxide Fusion, Chrome Iron Ores " in chapter under Chromium.) Boil the filtrate for 30 minutes to expel the excess of peroxide, make acid with 50 ml. of H_2SO_4 (1 : 3) in excess, cool, dilute to a volume of about 500 ml. with cold water, add a measured excess of ferrous ammonium sulfate solution, more than sufficient to completely reduce the chromium and titrate back with the standard $KMnO_4$ solution.

Proceed as in " Determination of Chromium, Analysis of Nichrome."

Determination of Molybdenum

Method.—Dissolve 0.5 g. of the sample in a 250-ml. beaker with 30 ml. of HCl (sp.gr. 1.18) and 30 ml. of HNO_3 (sp.gr. 1.42), evaporate to a volume of 20 ml., add 5 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of H_2SO_4. Cool, add 2 ml. of water and fume a second time. Cool, dilute to 50 ml. with water, bring to boiling to dissolve salts, filter and wash with hot water. Reserve the filtrate. If the residue contains undissolved alloy, transfer to a porcelain crucible, dry, ignite at a low heat, cool, transfer to a small nickel crucible and fuse with 10 times its weight of a mixture of equal parts of Na_2O_2 and Na_2CO_3. Cool, leach with least amount of water, filter and wash. Discard the residue. Boil the filtrate 30 minutes to expel the excess of peroxide, make slightly acid with H_2SO_4 (1 : 1) and boil to expel CO_2. Combine with the main filtrate.

Bring the combined solutions to boiling and pass H_2S for 15 minutes. The volume at this point should not exceed 175 ml. Transfer to a 250-ml. pressure flask, stopper and immerse in hot water for 45 minutes. Let stand over night. Filter on a 9-cm. filter and wash with cold dilute H_2SO_4 (1 : 50) through which H_2S has been passed. Dissolve any adhering precipitate in the flask and on the tube used for passing the H_2S gas with 10 ml. of hot HNO_3 (sp.gr. 1.42), wash into a 250-ml. beaker, add the filter paper containing the precipitate, then add 5 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of H_2SO_4, taking the

necessary steps to remove carbonaceous matter and the last traces of nitric acid. (See " Determination of Lead, Bismuth, etc. in Tin Base Bearing Metal.") Cool, add 75 ml. of water and boil to a clear solution. Partially reduce the molybdenum with 5 g. of granulated zinc and proceed as in " Determination of Molybdenum in Wulfenite or Molybdenite " in chapter under Molybdenum.

DETERMINATION OF MANGANESE [33]

Solutions Required. ***Ferrous Ammonium Sulfate and 0.1 N $KMnO_4$ Solution.***—See " Determination of Chromium, Analysis of Nichrome." (Each milliliter of 0.1 N $KMnO_4$ equals 0.0027465 g. of manganese.)

Method.—Weigh 2 g. of the sample into a 600-ml. beaker, add 30 ml. of HCl (sp.gr. 1.18) and 30 ml. of HNO_3 (sp.gr. 1.42) and heat until dissolved. If the residue remaining contains undissolved alloy, dilute, filter and wash. Transfer the residue to a porcelain crucible, dry, ignite at a low heat, cool, transfer to a small pure iron crucible, fuse with 10 times its weight of Na_2O_2, cool, leach with least amount of water, remove and wash the crucible, make the solution acid with HNO_3 (sp.gr. 1.42) and boil to expel H_2O_2. Combine this recovered portion with the main filtrate and evaporate the combined solutions to a syrupy consistency. Take up with 50 ml. of HNO_3 (sp.gr. 1.42), evaporate as before, add 100 ml. of HNO_3 and boil down to a volume of 80 ml. Add 3 g. of $KClO_3$ in portions of 0.5 g. each and boil at least 5 minutes after the last addition of the $KClO_3$. Add 100 ml. of water, filter through a thin asbestos pad with suction and wash thoroughly with dilute HNO_3 (1 : 200). Transfer the pad and precipitate to the original beaker being sure to recover any precipitate adhering to the funnel.

Now add 100 ml. of water, 50 ml. of H_2SO_4 (1 : 3) and a measured amount of ferrous ammonium sulfate solution, slightly more than sufficient to dissolve the MnO_2 (about 20 ml. should suffice). When the MnO_2 is completely dissolved, titrate the excess of ferrous ammonium sulfate solution with the standard $KMnO_4$ solution.

Ascertain as in " Determination of Chromium, Analysis of Nichrome " the number of milliliters of standard $KMnO_4$ solution that would be required to titrate an amount of ferrous ammonium sulfate solution equal to that added to dissolve the MnO_2. The difference between the number of milliliters of $KMnO_4$ solution calculated and the number used for the titration of the sample represents the manganese present and the percentage is found by multiplying this volume by 50 times the manganese titre of the $KMnO_4$ solution.

DETERMINATION OF SILICON

Method.—Proceed as in " Determination of Silicon, Analysis of Nichrome."

[33] See "Ford-Williams Method for Manganese" in chapter under Manganese; also. Proc. A. S. T. M., Part I, p. 598, 1929.

TENTATIVE METHODS OF CHEMICAL ANALYSIS OF PIG LEAD.

A. S. T. M. METHOD [34]

SERIAL DESIGNATION: B 35–36T [35]

A. DETERMINATION OF SILVER

Weigh 100 g. of the sample into a 3-in. scorifier and heat in a muffle furnace until the assay "covers." Pour into an iron mold and allow to cool. Free the resulting lead button from PbO, scorify again and pour as before. The button last obtained should not weigh over 20 g. and can be cupelled directly. Weigh the silver button obtained upon an assay balance.

NOTE.—If the amount of silver is large, the button should be examined for gold, in the usual manner.

B. DETERMINATION OF BISMUTH

Solutions Required. ***Sodium Carbonate.***—Dissolve 100 g. Na_2CO_3 in a liter of distilled water.

Ammonium Carbonate.—Make a half saturated solution.

Alkaline Sulfide Wash Solution.—Dissolve 200 g. of KOH in a liter of distilled water and mix one part of this solution with 4 parts of H_2S water.

Method. (*a*) ***Determination for Ordinary Amounts of Bismuth.***—Dissolve 20 g. of the sample in a 400-ml. beaker with 100 ml. of HNO_3 (1 : 4), with the aid of heat. When solution is complete, add dilute ammonia (1 : 2) with constant stirring, drop by drop from a burette, until a faint opalescence appears. If an actual precipitate is formed, redissolve by the addition of a small amount of HNO_3 (1 : 4) and repeat the addition of ammonia. Now add 5 ml. of HCl (1 : 9), fill the beaker with hot water, bring to boiling, and allow to stand on a steam bath for two hours. The assay, while standing, must not reach the boiling temperature. Filter through a 7-cm. paper. Transfer the precipitate completely to the paper by means of a "policeman" and wash twice with hot water. Carefully examine the filtrate, washings, and any decanted liquid and reject if clear. Dissolve the precipitate by dropping around the edges, from a 5-ml. pipette, 5 ml. of boiling HCl (1 : 9), receiving the solution in the original beaker. Wash the paper thoroughly with hot water, fill the beaker with water, bring to boiling, and allow to stand as before. Filter the bismuth oxychloride upon a weighed Gooch crucible, wash thoroughly with water, once with alcohol, once with ether, and dry upon the hot plate. Cool and weigh.

NOTE.—If time permits it is convenient to allow the assay to stand over night. In that case, the precipitate of bismuth oxychloride generally settles so completely that the clear supernatant solution can be decanted.

[34] This method is reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St. Philadelphia, Pa.

[35] These methods are issued under the fixed designation B 35; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1919; Adopted, 1920; Revised, 1924; Reverted Tentative, 1936. See A. S. T. M. Methods of Chemical Analysis of Metals, p. 174. December, 1936.

(*b*) ***Determination for Amounts of Bismuth Smaller than Can be Determined by*** (*a*).—Dissolve 100 g. of the sample in 500 ml. of dilute HNO_3 (1 : 4). When solution is complete, allow to cool and add Na_2CO_3 solution little by little until a slight permanent precipitate has formed. Then add 50 ml. of the Na_2CO_3 solution, bring to boiling, allow to stand warm until the supernatant liquor is clear again, filter and reject the filtrate. Dissolve the precipitate without washing by slowly pouring hot HNO_3 (1 : 4) around the edges of the filter paper, using no more acid than necessary. Wash the paper once with hot water and determine bismuth in the filtrate as described in (*a*).

NOTE.—When the sample contains a small amount of bismuth, it is often difficult to ascertain when the correct amount of ammonia has been added to the nitrate solution. In this case, place a small piece of litmus paper in the solution, and add the ammonia very gradually until the litmus paper indicates a neutral reaction.

(*c*) ***Determination of Bismuth in Samples Containing Appreciable Amounts of Tin and Antimony.***—Use a piece of litmus paper as in Note under (*b*), and after the first precipitation of bismuth oxychloride has been filtered off and washed (see (*a*)) proceed as follows: Dissolve the bismuth by dropping around the edges of the paper 10 ml. of boiling HCl (1 : 2), receiving the solution in the original beaker. Discard the paper after washing. Dilute the solution to about 200 ml. with fresh H_2S water and then pass H_2S gas through the hot solution for 15 minutes. Filter and wash with hot water. Remove any tin or antimony present by washing three times with alkaline sulfide wash solution. Wash the precipitate again with hot water, place it, together with the filter paper, in a 100-ml. beaker, add 20 ml. of HNO_3 (1 : 4), boil until sulfides are completely dissolved and the paper well pulped. Filter the solution, receiving the filtrate in the original beaker, and wash well. Determine bismuth in the original beaker, and wash well. Determine bismuth in the filtrate as in (*a*).

NOTES.—When the sample contains comparatively large amounts of tin or antimony, the residue left after the solution of the lead in the nitric acid obscures the opalescence found upon the addition of ammonia.

If the original sample contains more than 0.25 per cent of bismuth, it is preferable to use only a 10-g. charge.

C. DETERMINATION OF ARSENIC

Method.—Dissolve 111.11 g. of the sample in 550 ml. of HNO_3 (1 : 4). When solution is complete wash into a graduated liter flask, add 75 ml. of H_2SO_4 (1 : 1), cool, and make up to the mark with water. Transfer to a large beaker, rinsing out the flask with 25 ml. of water. Mix thoroughly, allow to settle and filter off 900 ml., equivalent to a 100-g. charge. Evaporate in a large porcelain dish until only enough H_2SO_4 is left to moisten the residue. When cool, wash into a small distilling flask with 60 ml. of HCl (sp.gr. 1.18) and 20 ml. of water, cleaning the dish carefully. Add 10 g. of ferrous sulfate and distill, boiling to as small a volume as possible. When cool add 50 ml. more of HCl (sp.gr. 1.18) and redistill. Pass H_2S gas through the cold distillate for 45 minutes. Filter, and weigh the As_2S_3 on a Gooch crucible, washing with cold water, alcohol and CS_2. After drying and weighing, redissolve with $(NH_4)_2CO_3$ solution and reweigh the Gooch crucible, calculating the loss in weight to arsenic.

NOTE.—The 25 ml. of water added is equivalent to the volume of precipitated lead sulfate.

D. DETERMINATION OF REMAINING METALS

Solutions Required. *Tartaric Acid.*—Dissolve 50 g. of tartaric acid in 250 ml. of distilled water to which has been added 250 ml. HCl (sp.gr. 1.18).

Method.—Dissolve 222.23 g. of the sample in 1100 ml. of HNO_3 (1 : 4), using a 1300-ml. beaker. When solution is complete examine for color and turbidity. If clear, wash the solution at once into a 2000-ml. graduated flask. In case of a residue (Note 1), however, dilute to about 1100 ml. and allow to stand until the supernatant liquor is clear. Decant as much as possible into a 2000-ml. flask, filter the remainder and receive the filtrate in the same flask. Wash the precipitate well and then place it, together with the filter paper, in a 100-ml. beaker and add 20 ml. of the tartaric acid mixture. Heat to boiling and when the paper is well pulped allow to digest warm for 30 minutes. Now add 50 ml. of hot water, filter and wash. (Note 2.) Carefully dry the residue and ignite. If any appreciable residue remains, brush it into a small silver dish containing 1 g. of molten KOH. Fuse for 5 minutes, and after cooling dissolve in as little hot water as possible and add to the above mentioned tartaric acid filtrate. Render this solution just alkaline with ammonia and then just acid with HCl, and saturate hot with H_2S gas. After digesting for 30 minutes on the steam bath, pass H_2S through the solution again for 15 minutes. Filter and wash with slightly acidified H_2S water. Reject the filtrate. Wash the sulfides from the paper into the original beaker and add 5 ml. of KOH solution (1 : 5) for every 25 ml. volume present. Digest hot for 5 minutes and filter through the original paper into a small flask graduated to 110 ml. After washing with H_2S water containing a little of the KOH solution, cool the filtrate and make up to the mark. Mix and reserve 100 ml. as alkaline sulfide solution No. 1. The precipitate may be discarded.

Add slowly to the main solution in the 2000-ml. flask 150 ml. of H_2SO_4 (1 : 1). After cooling and filling up to the mark, pour into a clean 3-liter flask provided with a rubber stopper. Rinse the flask out with 50 ml. of water, which is equivalent to the volume of lead sulfate present and is added to the portion. After mixing thoroughly by shaking, allow the precipitate to settle and filter off 1800 ml. of the liquid. This is equivalent to a 200-g. charge. Place this in a No. 9 porcelain evaporating dish and evaporate, first over a free flame and later on the hot plate until only enough H_2SO_4 is left to moisten the residue remaining. Add 50 ml. of water and, after digesting warm for a short time, wash the solution into a 250-ml. beaker, cleaning the dish carefully. Allow the solution to digest on the steam bath for 4 or 5 hours. (Note 3.) Then filter, wash and evaporate the filtrate to 200 to 250 ml. Place any residue (Note 4), together with the filter paper, in a 100-ml. beaker and treat with 20 ml. of the tartaric acid mixture. Boil for 5 minutes, dilute with 50 ml. of hot water and filter. Make the filtrate alkaline with ammonia and just acid with HCl, and obtain the tin, antimony and arsenic as previously described, reserving the whole of the alkaline sulfide solution as solution No. 2. Reject the sulfide residue.

To filtrate from the lead sulfate, add ammonia until the neutral point is reached, and then for every 50 ml. of the solution present add 2 ml. of HCl (sp.gr. 1.18). Pass H_2S gas into the hot solution until saturated, digest for 30 minutes on the steam bath and again pass H_2S gas into the solution. Filter

and wash with H_2S water slightly acidified. (Note 5.) Separate tin, antimony and arsenic in the precipitate with KOH solution as usual, obtaining an alkaline sulfide solution No. 3. (Note 6.)

To sum up, three alkaline sulfide solutions have been obtained, containing tin, antimony and arsenic, a precipitate of metallic sulfides containing copper, lead, etc., and a solution containing iron, zinc, nickel, etc.

NOTES.—1. A residue indicates the presence of antimony, tin, possibly arsenic, or sulfur as lead sulfate.

2. It has been found that even this treatment occasionally fails to dissolve stannic acid completely.

3. If it is preferred, allow the solution to stand over night to insure the complete solution of all soluble salts.

4. Any residue of lead sulfate may contain some tin, antimony, or possibly arsenic.

5. The filtrate will contain any iron, zinc, nickel, cobalt and manganese; while in the precipitate will be found any copper, cadmium, lead, silver, bismuth, tin, antimony and arsenic.

6. When separating the sulfides of arsenic, antimony and tin from sulfides of copper, lead, etc., it is necessary to wash all the sulfides back into the beaker in which they were precipitated. These sulfides sometimes cling so tenaciously to the paper that in dislodging them more water than the 25 ml. specified is required. In this case allow the sulfides to settle and then decant the clear supernatant liquor through the filter until the volume is reduced to 25 ml. Before rejecting the decanted fluid always test with H_2S water.

In washing sulfide precipitates with water, much trouble is experienced from the tendency of the precipitate to pass through the filter in the colloidal form. This is particularly true in washing sulfides that have been digested with KOH. Time and trouble will be saved by washing all the sulfides precipitated from mineral acid solutions with H_2S water containing a little of the acid in which they were precipitated. The same is true of sulfides precipitated in or filtered from an alkaline solution.

When working with alkaline solutions in which tin is to be determined, avoid the use of Jena or other glass that contains zinc. The zinc content of the glass may influence the result.

DETERMINATION OF ANTIMONY AND TIN

Solutions Required. ***Potassium Iodide.***—Dissolve 100 g. in a liter of distilled water.

Standard Sodium Thiosulfate.—Dissolve 24.8 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 1000 ml. of distilled water, and allow to stand for 24 hours. Standardize against Antimony Metal c.p., using the same quantity of reagents and same procedure as under method. Each milliliter is equivalent to approximately 0.006 g. of antimony.

Method.—Wash the alkaline sulfide solutions Nos. 1, 2, and 3 into a 600-ml. beaker, and acidify with 5 ml. of HNO_3 (sp.gr. 1.42) and 20 ml. of HCl (sp.gr. 1.18). Evaporate the solution to dryness on the steam bath. To the residue add 200 ml. of water, 10 g. of oxalic acid and 10 g. of ammonium oxalate and heat the solution until it is clear. Then pass H_2S gas through the boiling solution for 45 minutes. Filter off the precipitate, consisting of arsenic and antimony sulfides, and wash with hot water. Determine tin electrolytically in the filtrate, continuing the electrolysis until all the oxalic acid is decomposed and the solution becomes alkaline. Dissolve the deposit on the cathode with a small amount of HCl and examine qualitatively for tin.

Dissolve the sulfides of arsenic and antimony in KOH as usual, collecting the filtrate in a 500-ml. Erlenmeyer flask. Add 50 ml. of HCl (sp.gr. 1.18)

and boil the solution until about 30 ml. are left. Expel the arsenic as chloride. Now oxidize the solution with a pinch of $KClO_3$ and boil until no more chlorine remains. Cool and add 5 ml. of potassium iodide solution. Titrate the liberated iodine with 0.1 N sodium thiosulfate solution, using carbon disulfide as an indicator.

DETERMINATION OF COPPER AND CADMIUM

Solutions Required. ***Sodium Chloride*** (***Solution No. 1***).—Dissolve 1 g. of NaCl in 100 ml. of distilled water.

Sodium Chloride (***Solution No. 2***).—Dissolve 10 g. of NaCl in 100 ml. of distilled water.

Standard Potassium Cyanide.—Dissolve 2 g. of KCN in a liter of distilled water and standardize against a known amount of copper as treated in the analysis.

Sodium Carbonate (***Solution No. 1***).—Dissolve 50 g. of Na_2CO_3 in 1 liter of distilled water.

Sodium Carbonate (***Solution No. 2***).—Dissolve Na_2CO_3 in distilled water to saturation.

Method. (*a*) ***Determination Where Copper Exceeds 0.0025%.***—Place the filter containing the sulfides in a 100-ml. beaker and add 20 ml. of HNO_3 (1 : 4). Heat with occasional stirring until the paper is thoroughly pulped and the sulfides are completely dissolved. Filter into a 250-ml. beaker. Dry the residue, which generally contains a small amount of copper, ignite in a porcelain crucible, boil with 5 ml. of HNO_3 (1 : 1), and wash into the main portion, keeping the volume below 100 ml. Render it strongly alkaline with ammonia, and add 5 g. of potassium cyanide, then saturate it in the cold with H_2S gas. (Note 1.) Filter the solution and evaporate the filtrate to a volume of 20 to 30 ml. in a 4-in. porcelain casserole. Boil until solution is complete. Add 20 ml. of H_2SO_4 (1 : 1) and evaporate the solution under a hood until dense fumes of H_2SO_4 escape. Cool, dilute, and warm until copper sulfate is all dissolved. Now filter, if necessary, into a 200-ml. beaker, render just alkaline with ammonia, make acid by the addition of 3 ml. of HNO_3 per 100 ml. of solution, and electrolyze for copper.

Dissolve the precipitate of sulfides in the usual manner with 20 ml. of HNO_3 (1 : 4). Add 1 ml. of NaCl solution No. 1 to the solution, still containing the pulped filter, and digest for 30 minutes. Filter off the AgCl, wash and reject. Make the filtrate, not exceeding 100 ml., alkaline with a slight excess of Na_2CO_3 and add 5 g. of KCN. Digest for 1 hour. Filter and wash with Na_2CO_3 solution No. 1. Reject the precipitate of bismuth. Now add a few milliliters of ammonium sulfide solution to the filtrate to precipitate any cadmium as yellow cadmium sulfide. Filter upon a weighed Gooch crucible and weigh as cadmium sulfide. (Note 2.)

NOTES.—1. Copper remains in the solution, while lead, silver, bismuth and cadmium are precipitated.

2. If an appreciable amount of cadmium sulfide is found, it should be converted to and weighed as cadmium sulfate, according to method for cadmium under "Determination as Sulfate" in chapter under Cadmium.

(*b*) ***Determination Where Copper is Less than 0.0025%.***— Place the paper containing the sulfides in a porcelain crucible, dry carefully and ignite.

When the carbon has been all burned off, cool and dissolve the residue in 5 to 10 ml. of HNO_3 (1 : 1). After evaporating to a volume of 1 to 2 ml. add 1 ml. of H_2SO_4 (1 : 1). Then evaporate the solution until fumes appear, cool, dilute, add a few drops of NaCl solution No. 2, and filter off the lead sulfate and silver chloride. Again evaporate the filtrate until fumes of H_2SO_4 appear, and when cold dilute and neutralize with Na_2CO_3 solution No. 2. Then add about six drops of concentrated ammonia and titrate the solution with standard KCN solution until the blue color is discharged.

The cadmium can be obtained by making this solution, titrated for copper, strongly alkaline, diluting a little, and adding 5 g. of KCN. Saturate the solution cold with H_2S gas, filter, discard the filtrate and treat the precipitate for cadmium as described in Method (*a*).

DETERMINATION OF IRON

Method.—Evaporate the filtrate containing iron, zinc, etc., to 100 ml. and oxidize with a few drops of HNO_3. Separate the iron with ammonia as usual, making two separations, and receive the filtrate in a 500-ml. Erlenmeyer flask. Redissolve the iron hydroxide with hot HCl (1 : 1) or dilute H_2SO_4 and determine the iron volumetrically by any of the standard methods.

DETERMINATION OF ZINC

Solutions Required. ***Nitric Acid*** *(1 : 4).*—Mix 200 ml. of HNO_3 (sp.gr. 1.42) with 800 ml. of distilled water.

Sulfuric Acid *(1 : 1).*—Carefully pour, with stirring, 500 ml. of H_2SO_4 (sp.gr. 1.84) into 500 ml. of distilled water.

Acidulated Hydrogen Sulfide Water.—Add 20 ml. of HCl (sp.gr. 1.18) to 1000 ml. of distilled water and saturate with hydrogen sulfide.

Ammonium Thiocyanate Solution *(2%).*—Dissolve 20 g. of NH_4CNS in 1000 ml. of distilled water.

Hydrochloric Acid *(1 : 3).*—Mix 100 ml. of HCl (sp.gr. 1.18) and 300 ml. of distilled water.

Standard Zinc Solution *(0.1 mg. of zinc per ml.)*—Dissolve exactly 0.1 g. of U. S. Bureau of Standards pure zinc in 5 ml. of HCl (sp.gr. 1.18) and dilute to exactly 1000 ml. with distilled water.

Potassium Ferrocyanide Solution.—Dissolve 34.8 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ in 1000 ml. of distilled water.

Method.—Dissolve 222.23 g. of the sample in 1100 ml. of HNO_3 (1 : 4), using a 1300-ml. beaker. When the lead is dissolved, transfer the solution to a 2000-ml. graduated flask and add slowly 150 ml. of H_2SO_4 (1 : 1). Cool, fill the flask to the mark and then pour the solution into a clean 3000-ml. flask provided with a rubber stopper. Rinse the measuring flask with exactly 50 ml. of water, which is equivalent to the volume of lead sulfate which is present. Mix the solution thoroughly by shaking, allow the precipitate to settle and filter through a dry filter until 1800 ml. of filtrate has been obtained.

Place exactly 1800 ml. of filtrate (equivalent to a 200-g. charge) in a No. 9 porcelain evaporating dish and evaporate the solution to approximately 100 ml. Transfer the solution to a 600-ml. beaker, neutralize with ammonia, and then add 5 ml. of HCl (sp.gr. 1.18) for every 100 ml. of solution. Warm the solution and pass in a rapid current of hydrogen sulfide until it is saturated. Digest for 30 minutes on the steam bath, add an equal volume of water and again saturate with hydrogen sulfide. Filter and wash with acidulated H_2S water.

Discard the precipitate and evaporate the filtrate in glassware containing no zinc until the volume of the solution is approximately 100 ml.

Neutralize the solution with ammonium hydroxide, add 5 g. of citric acid, and warm until the acid is dissolved. Add small portions of calcium carbonate to the hot citric acid solution until about 1 g. of calcium citrate has separated and then pass in a rapid current of H_2S as the solution is allowed to cool. Allow the solution to stand for from 2 to 4 hours, part of the time on a water bath, until the supernatant liquid is clear.

Collect the precipitate on a filter, wash with a 2% solution of ammonium thiocyanate and then dissolve the precipitate in hot dilute hydrochloric acid (1 : 3). If the solution has a reddish color (due to iron) the zinc must be reprecipitated as above. If the solution is clear, evaporate it to dryness on the steam bath, take up the residue in 3 ml. of HCl (sp.gr. 1.18), add 20 ml. of water and filter if not perfectly clear.

Transfer the solution (Note 2) to a 100-ml. Nessler jar and dilute to 95 ml. Prepare other Nessler jars containing 3 ml. of HCl (sp.gr. 1.18) and definite volumes of standard zinc solution. Dilute to 95 ml. Add 5 ml. of potassium ferrocyanide solution to each jar, mix quickly, and compare the turbidities by viewing longitudinally as the jars are held over a sheet of fine print. Add more of the standard zinc solution from a burette to the jar which approximates the turbidity of the unknown most closely, until the turbidities match each other and calculate the percentage of zinc on the basis of a 200-g. sample or the aliquot portion taken.

NOTES.—1. All glassware that contains zinc must be avoided and in umpire work a blank test should be carried along with the test.

2. The whole solution can be used if the lead contains no more than 0.00025% of zinc. If more zinc is present it is best to take such an aliquot portion of the solution as will give approximately 0.5 mg. of zinc and then to add enough HCl to provide 3 ml.

3. For further details concerning the turbidmetric test, consult the "Determination of Small Quantities of Zinc" by Mr. Bodansky, in the *J. Ind. Eng. Chem.* **13**, pp. 696–697 (1921).

4. The addition of calcium carbonate with the formation of a precipitate of calcium citrate serves the purpose of giving a clear filtrate, and prevents the loss of colloidal sulfide.

DETERMINATION OF NICKEL AND COBALT

Solutions Required: ***Hydrogen Sulfide Wash Water.***—To each 100 ml. of hydrogen sulfide water add 20 ml. neutral ammonium acetate.

Method.—Render the filtrate just alkaline with ammonia and saturate with H_2S. Heat to boiling and then make just acid with acetic acid, add 20 ml. of neutral ammonium acetate solution, and boil until the sulfides of nickel and cobalt separate out. Filter and wash with warm H_2S wash water. Dry the

precipitate and paper in a porcelain crucible and carefully ignite. If there is an appreciable amount of residue after ignition, dissolve by boiling with 10 ml. of aqua regia, wash into a 250-ml. beaker, add 10 ml. of H_2SO_4 (1 : 1), evaporate until fumes appear, cool, dilute to 200 ml., make alkaline with ammonia, and add 15 ml. of concentrated ammonia. Then electrolyze the solution and weigh the nickel and cobalt as such.

NOTES.—If the amount of nickel and cobalt is small it can be weighed as oxide.

If the filtrate from the nickel and cobalt sulfides shows a brown color, it indicates that the precipitation has not been complete. In this case render the solution ammoniacal and repeat the above process.

ALLOYS, II

THE CHEMICAL ANALYSIS OF IRON AND STEEL [1]

INTRODUCTION

The former division of the subject of steel analysis into the fields of plain carbon steels and alloy steels is no longer followed in the better treatises in this field. Due to the cooperation of the National Bureau of Standards and the various industrial laboratories and societies for the standardization of methods of testing, the referee methods in this field are now well standardized, and for this reason the subject of steels and ferroalloys is now covered by reproducing the methods of the American Society for Testing Materials. There are included in this chapter some selected methods for various elements, under the caption " Other Methods " (p. 1470). Those who desire a still fuller selection of methods should consult one of the more extended treatises in this field.[2] The present selection should serve for all practical purposes.

TENTATIVE METHODS OF CHEMICAL ANALYSIS OF STEEL, CAST IRON, OPEN-HEARTH IRON AND WROUGHT IRON [3]

A. S. T. M. Designation: E 30–36 T [4]

PREFACE

The following methods have been compiled as standard procedures for use in referee analyses. These methods, however, are not intended to preclude the use of other methods (or apparatus) that give results within the permissible tolerances. In any case, the analyst should check the method and technique

[1] Methods from the literature; arranged by N. H. Furman.

[2] Lundell, Hoffman and Bright, Chemical Analysis of Iron and Steel, J. Wiley & Sons, Inc., 1932. New York. C. M. Johnson, Chemical Analysis of Special Steels, John Wiley & Sons, Inc., New York, 1930. Methods of the Chemists of the U. S. Steel Corporation, published by the Carnegie Steel Co., Pittsburgh, Pa. W. W. Scott, Technical Methods of Metallurgical Analysis, D. Van Nostrand Co., New York, 1923. F. Ibbotson, The Chemical Analysis of Steel-Works Materials, Longmans Green & Co., New York, 1920.

[3] Under the standardization procedure of the Society, these methods are under the jurisdiction of the A. S. T. M. Committee E-3 on Chemical Analysis of Metals. Reproduced with the permission of the American Society for Testing Materials, 260 S. Broad St. Philadelphia, Pa.

[4] This is a *Tentative Standard* and under the Regulations of the Society is subject to annual revision. Suggestions for revision should be addressed to the Headquarters of the Society, 260 S. Broad St., Philadelphia, Pa. Issued, 1936. Accepted for publication as tentative by Committee E-10 on Standards, August 26, 1936.

that is used by means of a National Bureau of Standards' standard sample that has a composition comparable with that of the material under test. A list of these Standard Samples is given in the Bureau's Supplement to Circular 398.

Concentration of Acids.—Throughout these methods, the use of concentrated acids is intended, unless otherwise specified. For example, hydrochloric acid, or HCl, refers to the concentrated acid (sp.gr. 1.18) as furnished by the manufacturers. Diluted acids will be designated as in the following example, " diluted HCl (2 : 98) " will mean 2 volumes of the concentrated acid of sp.gr. 1.18 diluted with 98 volumes of water.

Water.—The term " water " as used in these methods refers only to distilled water.

PRECAUTIONS

Attention is directed to certain precautions to be observed in the use of the reagents employed in the analytical procedures described in these methods.

Perchloric acid has become a valuable reagent in the analysis of ferrous alloys. While perchloric acid of 70% strength may be boiled with impunity at approximately 200° C., it cannot be too strongly emphasized that contact *of the boiling undiluted acid or hot vapor* of perchloric acid *with organic matter*, or even easily oxidized inorganic matter such as compounds of trivalent antimony, will lead to serious explosions. If oxidizable substances are present, *nitric acid must always be added* as a precautionary measure *before evaporating to fumes of perchloric acid.* Do not use rubber thumb stalls around fuming perchloric acid. Handle with beaker tongs. Perchloric acid evaporations should be done in a hood with good draft. Hoods with wood frames in which a great deal of $HClO_4$ is fumed should be washed occasionally with water.

Hydrofluoric acid burns are both painful and dangerous, as infection and necrosis of bone tissue may occur. If hydrofluoric acid has touched the skin wash immediately with plenty of water and soak the exposed part in a strong solution of borax.

Nitric dioxide vapors are cumulatively harmful to the respiratory system so solutions of metals in nitric acid should be made in a well-ventilated hood.

Hydrogen sulfide is a dangerous poison which is fatal if inhaled in sufficient concentrations. Precipitations and filtrations involving this reagent should be done under the hood.

SAMPLING

(*a*) **Rolled and Forged Steel Products.**—Different parts of a piece of steel vary in composition. For this reason, a sample from a single piece must be carefully selected if it is to be representative of that piece. If the analysis is to be representative of the melt, a number of representative pieces should be sampled and analyzed separately. In any case, the sample shall be so selected as to be thoroughly representative, and large enough to suffice for all of the required determinations.

It should be remembered that the composition of the steel is changed by certain operations and that samples should be taken from the steel in its original condition.

Preparation of Samples.—Samples shall consist of drillings or chips cut by some machine tool without the application of water, oil, or other lubricant,

and shall be free from scale, surface metal, grease, dirt, or other foreign substances. If the samples are taken by drilling, a drill not less than ½ nor more than ¾ in. in diameter shall be used. Samples shall be uniform, thoroughly mixed, and free from dust. Chips too coarse to pass a No. 20 sieve are not recommended, nor shall long curly drillings which will not pack closely for the carbon determination be used.

In referring samples to other analysts for check analyses, pieces of the original full-size section, when possible, should be submitted rather than cuttings, unless the latter are specifically requested.

Location of Samples: Large Sections.—For large sections, including blooms, billets, slabs, rounds, squares, shapes, etc., samples shall be taken at any point midway between the outside and the center of the piece by drilling parallel to the axis. In cases where this is not practicable, the piece shall be drilled on the side, see Fig. 183 (*b*) and (*c*), but the drillings shall not be collected until they represent the portion midway between the outside and the center. The tension test specimen may be used for sampling if it conforms to the above conditions.

Bored Forgings.—For bored forgings, samples shall be taken midway between the inner and outer surface of the wall.

Thin Material.—For thin material or material of small cross-section, such as plates, shapes, bars, etc., if the method described above for large sections is not applicable, the sample shall be taken by machining off the entire cross-section, or, if this is not possible, by drilling entirely through the material at a point midway between the outside and the center, See Fig. 183 (*a*).

Sheets Rolled Longitudinally.—For sheets rolled from slabs or bars longitudinally, the specimen for sampling shall be cut 2 in. in width and across the full width of the sheet as rolled. The specimen shall be cleaned by pickling or grinding and then folded once or more by bringing the ends together and closing the bend. The sample for analysis shall be taken in the middle of this length by milling the inside sheared edges or drilling entirely through from the flat surface. Sampling by milling is preferable. For sheets of a light gage more than one specimen may be taken and stacked together before folding.

Sheets Rolled Transversely.—For sheets rolled from slabs or bars transversely, the specimen shall be cut from the side of the sheet, half way between the middle and end as rolled, 2 in. in width and 18 in. in length. If the sheet is No. 20

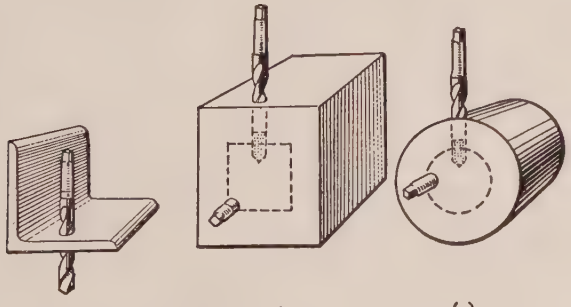


Fig. 183.—Location of Samples for Check Analysis.

gage (24 oz. per sq. ft. or 0.037 in. in thickness) or lighter, the specimen shall be cut from the full length of the sheet as rolled. The specimen selected shall be cleaned by pickling or grinding and then folded once or more by bringing the ends together and closing the bend. The sample for analysis shall be taken in the middle of this length by milling the inside sheared edges or drilling entirely through from the flat surface. Sampling by milling is preferable.

Sheets Not of the Full Size, Rolled.—Sheets cut from larger sheets and not of the full size rolled shall be sampled by milling or drilling the sheet in a sufficient number of places so that the sample is representative of the entire sheet. The sampling may be facilitated by folding the sheet both ways.

(*b*) **Pig Iron.**—In the absence of a special agreement between the manufacturer and the purchaser, or whenever it is necessary to sample pig iron in the solid state, the sampling shall be carried out in the following manner: Not less than 3 pigs shall be taken to represent any lot or shipment and for lots of more than 30 tons one pig shall be taken for each 10 tons of iron. The pigs shall be selected by some means such as the knotted rope system, that eliminates the element of personal choice; and 3 to 7 pigs taken in the order selected, shall constitute a unit sample. For boat or barge shipments arrangements between the seller and the purchaser may be made, if desired, in regard to taking fewer pigs per ton. If for any reason it is desirable to fracture the pigs, they may be broken in two, and one portion of each of the original pigs reserved for the sample for analysis. Any loose sand or other deleterious matter on the reserved portions shall be removed, conveniently by brushing.

The sample for analysis shall be collected after the proper discard, by drilling each pig or portion of pig with a properly sharpened and hardened, flat beaded, ⅝- or ¾-in. highspeed tool-steel drill in a direction at right angles to the long axis of the pig and at such a feed as to form a minimum amount of fine drillings. The first drillings shall be discarded and only the drillings collected after the drill is cutting into clean metal shall be reserved for the sample. The drilling shall extend to within ¼ in. of the opposite surface of the pig; and suitable precautions shall be taken to collect all the drillings, fine as well as coarse particles, and to avoid contamination of the sample in any way. Any pigs or portions of pigs found too hard to drill readily may be annealed by heating to a dark red color and cooling in air.

The sample for analysis shall be composed of equal portions by weight of the drillings from the pigs forming the unit sample, and the weight of the combined sample shall not be less than 75 g. The drillings shall be thoroughly mixed, as by gently grinding in a suitable mortar until all pass the No. 20 (840-micron) sieve.[5] Unless accurate determinations of combined and graphitic carbon are required, the sample shall be carefully divided into two or more portions by pouring in a cone-shaped pile on glazed paper and halving or quartering in the usual manner. These portions, of which one shall be reserved for the manufacturer and one for the purchaser, shall be placed in a suitable container, fully labeled for identification, and dispatched to the laboratories without unnecessary delay and with full instructions as to the determinations required.

[5] See Standard Specifications for Sieves for Testing Purposes (E 11-26), 1936 Book of A. S. T. M. Standards, Part II, p. 1413. Reproduced on pp. 1329–1333 of this Volume.

When combined and graphitic carbon must be determined with the highest degree of accuracy, equal portions by weight of the drillings from the pigs or parts of pigs representing a unit sample shall be mixed to form a sample of at least 100 g. which shall then be separated into coarse and fines by sieving as described under (*c*), the sampling of gray-iron castings.

(*c*) **Gray-Iron Castings.**—In accordance with the Standard Specifications for Gray-Iron Castings (A. S. T. M. Designation: A 48) of the American Society for Testing Materials,[6] three test bars, 1.20 in. in diameter shall be cast in sand from each heat after one quarter and three quarters of the heat has been poured.

One bar from each set having been broken, one end of each next to the fracture shall be thoroughly cleaned and the outer skin removed for a sufficient distance from the fracture and down to clean metal. Chips then shall be taken by means of a lathe or milling machine across the whole face of the bar until not less than 100 g. has been collected. The same amount shall be taken from each bar. The bar shall be so clamped as to permit the attachment or use of any suitable device for collecting every part of the sample and the machine shall be run slowly enough to reduce to a minimum the danger of loss of fine particles (avoid drafts). Horizontal drilling may also be employed.

Preparation of Samples from Castings for Analysis.—The entire gross sample shall be weighed and then sifted on a No. 80 (177-micron), and if need be a No. 120 (125-micron), tight-fitting sieve (with cover).[7] Both sieves and cover must be tight-fitting to avoid loss of fine graphite by dusting. As an alternate procedure (*a*) the drillings may be sifted through two sieves of such sizes that not under 10% nor more than 20% of the entire sample remains on the larger sieve, and not under 10% and not over 20% shall pass through the smaller sieve or (*b*) sieves may be used of such sizes that concordant results may be obtained.

The two (or three) portions so obtained shall be separately weighed. Each one shall then be thoroughly mixed without any loss of material and divided by weight into two (or three) exactly equal portions, each of which shall be placed in a clean, glass-stoppered bottle or other suitable receptacle and appropriately labeled. Of the three sets of the subdivided sample, one shall be placed in a clean, glass-stoppered bottle or other suitable receptacle and appropriately labeled. Of the three sets of the subdivided sample, one shall be retained by the manufacturer, one sent to the purchaser and one held in reserve.

Before weighing the sample for analysis, the contents of each bottle shall be thoroughly mixed. Carbon is determined on each of the sieved portions, and the carbon present in the original drillings is calculated from the ratio of the weights of the separate sieved fractions to the original iron.

As a general rule, the very fine material is richest in carbon, the coarse material next, while the intermediate sizes are the poorest. For routine analyses, the aim should be to obtain the iron in as small particles as possible, as for example by milling. In such case, the samples for graphite and carbon may be taken by forming a cone, flattening it out, and taking small dabs with

[6] 1936 Book of A. S. T. M. Standards, Part I, p. 457.

[7] See Standard Specifications for Sieves for Testing Purposes (E 11-26), 1936 Book of A. S. T. M. Standards, Part II, p. 1413.

a spatula from at least ten representative portions for each weighed portion. Less care is needed in taking portions for the determination of the other constituents; grab samples from the container after gentle tumbling are satisfactory.

(*d*) **Malleable Iron.**—Proceed as in the sampling of pig iron.

(*e*) **Wrought Iron.**—As it is desirable that the sample represent the entire cross-section of the specimen, sampling by milling is preferable. Specimens shall be freed from any mill scale by pickling, grinding, or other suitable means. It is necessary to secure *all* of the millings, for the various sized particles will differ in composition. For routine work, samples for carbon, manganese, phosphorus, sulfur, and silicon may be taken from the thoroughly mixed millings. For the determination of slag and oxides, or for umpire determinations of the other constituents, the entire sample shall be weighed and then sifted without dusting on a No. 35 (500-micron) sieve. The two fractions shall be weighed and in taking samples for analysis, portions of these two well-mixed fractions must be taken in the same proportion which they bear to the gross sample.

TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

The method of direct combustion of the metal in oxygen is recommended, the carbon dioxide obtained being absorbed in soda-asbestos with suitable purifying and protecting trains following the furnace. Owing to the diversity of apparatus by which correct results may be obtained in the determination of carbon, the recommendations are intended to indicate what is acceptable rather than to prescribe definitely what shall be used.

Apparatus and Reagents. ***Combustion Apparatus.***—Any combustion apparatus heated by electricity (preferably) or gas which will heat the sample to a temperature of 1000° to 1100° C. may be used. Electric furnaces, heated by silicon carbide rods giving temperatures up to 1370° C. are very useful for determining carbon in refractory alloys. Combustion tubes may be of porcelain, sillimanite, clay, quartz or platinum and obviously must be gas tight. Quartz is liable to devitrification when used intermittently at temperatures above 1000° C., and may then become porous. Tubes 30 in. in length with 1¼-in. inside diameter and drawn out at one end are convenient for the small Gooch crucibles of fused silica that are used in the determination of graphite.

Catalyzers.—Though materials such as ironized asbestos, copper oxide, platinized quartz or asbestos, or platinum gauze are often put in the exit end of the combustion tube for the purpose of insuring complete combustion of carbon to the dioxide, it is questionable whether they are of any value, save as baffles for holding back iron oxide dust and sulfur trioxide, for they soon become fouled. When such baffles are used the fixed sulfur shall be burned out every 200 determinations or oftener, by drawing the exit end of the combustion tube into the hot zone while a current of air or oxygen is passed through it. With high sulfur steels it is best to omit baffles in the exit end of the tube and insert a special sulfur dioxide absorber or purifier between the tube and the carbon dioxide absorber.

Boats and Covers.—The boats and covers may be of porcelain, quartz, alundum, clay, platinum or nickel, and should preferably receive a lining of granular alundum or any other material found to be suitable for the purpose.

Nickel boats shall not be made of sheet nickel containing more than 0.10% of carbon. Before use, new boats and covers shall always be preheated in oxygen until no more carbon dioxide is given off or until a constant blank is obtained. In order to prevent injury to the tube from spattering, a platinum or nickel cover open at both ends and allowing free access of oxygen is desirable.

Material for Lining Boats.—" RR Alundum " (Al_2O_3) alkali-free, specially prepared for carbon determinations, and 60-mesh or finer, is entirely satisfactory for the lining of boats. Ignited low-silica chrome ore, or " Zirkite " (natural oxide of zirconium) properly sized and freed from materials causing a blank may be employed. Ferric oxide has been recommended as permitting combustion at low (800° to 900° C.) temperatures but is not recommended for high temperatures. Quartz sand, owing to its liability to fuse or to slag with oxides of iron, causing bubbles of gas to be enclosed, is objectionable.

Oxygen.—The purity of the oxygen shall be not less than 99.5%. Organic matter of any kind is an undesirable impurity. It is usually absent, and it suffices to pass the oxygen through an absorbent such as soda-asbestos followed by anhydrone. If carbonaceous matter is suspected, the oxygen shall be passed through a tube that is loosely packed with asbestos or copper oxide and heated to about 450° C. before it is passed through the soda-asbestos.

Combustion of the Sample. *Size of Particles of Sample.*—The finer the chips (excluding dust, which causes low values on a hot boat), the better, except with alloys that burn too vigorously. Drillings or millings sized between 14 to 60 mesh are satisfactory.

Distribution of the Sample in the Boat.—In general, the sample shall be packed in a small groove or furrow that has been made in the bedding material in the boat. If the material burns too rapidly, satisfactory regulation of the speed of combustion may sometimes be obtained by spreading the sample somewhat loosely over the bedding material or by covering with a thin layer of the bedding material.

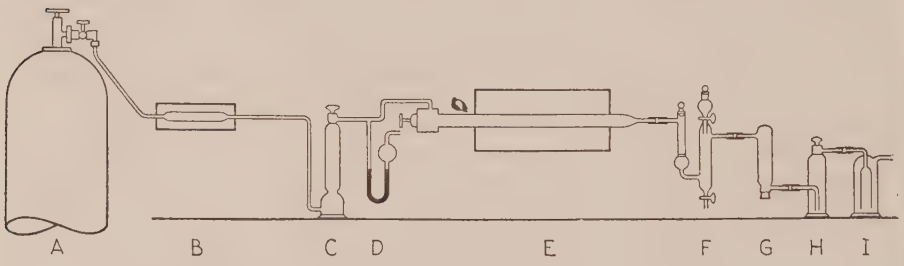
Addition of Accelerators to the Sample.—Shot tin, ⅛-in. pellets, is an excellent accelerator, one pellet being placed on each end of the layer of drillings. Millings of open-hearth iron, or other iron with 0.01 to 0.03% carbon are satisfactory aids in the combustion of large drillings and refractory alloys. Red lead, copper oxide, lead and powdered copper are also used. Red lead, unless previously ignited at 500° C. and kept in ground-glass stoppered bottles, will cause erratic blanks.

Preheating of Sample.—If the sample is allowed to come to the temperature of the furnace before the oxygen is admitted, it usually bursts into a bright flame and burns completely. A period of ½ to 1½ min. of preheating suffices.

Rate of Adding Oxygen.—The rate at which oxygen is admitted is also a factor in the velocity of combustion. Assuming the combustion apparatus has been heated to the temperature range above that recommended, it is possible, if the material is closely packed and if oxygen is admitted at too rapid a rate, that the combustion may be so violent as to cause excessive spattering of fused oxides and such fluidity of the molten slag that the boat or other container may be injured or destroyed. Sufficient oxygen, however, shall be run in *to insure a current of gas through the absorber at all stages of the combustion.* When tin is employed as an accelerator, combustion is very rapid and it is therefore necessary to increase the flow of oxygen during combustion. When the sample has

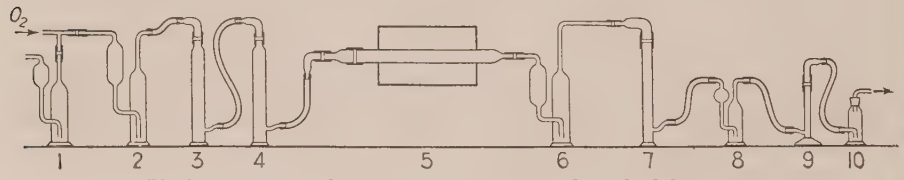
burned (1 to 2 min.) the flow of oxygen may be reduced to a rate of 150 ml. per min.

Purification of the Carbon Dioxide.—The purifiers that follow the combustion tube must remove finely divided oxides of iron, oxides of sulfur or selenium, dry the gases before they enter the weighed absorber, and protect the absorber from outside effects. Iron oxide is screened out during the passage of the gases through the liquids or columns of solids that precede the weighed absorber. The small amount of SO_2 that is given off from low-sulfur steels can be satis-



(*a*) Apparatus used at the National Bureau of Standards.

A. Oxygen tank with needle or reducing valve.
B. Preheating furnace, 450° C, with platinized asbestos.
C. Ascarite tower.
D. Mercury manometer.
E. Combustion tube and electric furnace, 1000–1150° C.
F. Special absorption tube which contains asbestos in the left arm, and in the right arm H_2SO_4 saturated with H_2CrO_4.
G. Tower with 20–30 mesh Anhydrone.
H. Weighed tower with Ascarite and Anhydrone.
I. H_2SO_4 guard tube and gage.



(*b*) Apparatus used in a representative steel-works laboratory.

1. Mercury valve.
2. Bottle containing concentrated H_2SO_4.
3. Tower, with gooseneck top, containing $CaCl_2$.
4. Tower with stick NaOH.
5. Electric furnace with combustion tube and adapters.
6. Bottle with aqueous solution of $KMnO_4$ (5%) inserted only for steels with more than 0.05% sulfur.
7. Tower with granulated zinc.
8. Bottle with concentrated H_2SO_4.
9. Tower with P_2O_5.
10. Weighed tower with Ascarite.

FIG. 184.—Apparatus for the Determination of Carbon by the Direct-Combustion Method.

factorily removed by H_2SO_4 that has been saturated with chromic acid. High-sulfur steels need other absorbents such as an aqueous solution of chromic acid (50%), a solution of $KMnO_4$ (5%), or heated platinized silica gel that will convert the dioxide to trioxide. The sulfur trioxide that is so formed is not removed by any one absorbent, but is condensed and absorbed during its passage through the liquids or columns of solids in the train.

Absorbing Bulbs.—No special types of absorbing bulbs are recommended, although the Fleming, Miller, Turner, and the Midvale (sometimes called Stetzer and Norton) bulbs have proved satisfactory. When filled, the tubes shall not weigh over 200 g. and they shall always be weighed filled with oxygen and against a like counterpoise. Open bulbs, such as the Midvale, lose oxygen by diffusion. They shall be filled with oxygen before weighing when not in continuous use, and the same time interval shall be held between weighings.

Absorbents.—The most desirable absorbent for carbon dioxide is 20 to 30 mesh soda asbestos (Ascarite) followed by Anhydrone, $Mg(ClO_4)_2$. The latter is needed to absorb the water which is formed during the reaction and is not held by the unused Ascarite.

General Arrangement of Apparatus.—Figures 184 (*a*) and (*b*) show two typical arrangements of the apparatus. The apparatus and arrangement may be modified, provided satisfactory results for the carbon determination will be obtained. For example, with oxygen free from carbonaceous matter the preheater may be omitted; other forms of absorption towers may also be substituted for the special absorption tube.

Procedure. ***Carbon Steel*** (***Sulfur Content less than 0.1%***).—After having properly set up and tested the apparatus, spread 1.36 to 2.73-g. of the sample on the bed material in the boat so that the particles are in intimate contact. Cover the sample with a suitable cover and introduce the boat into the hot combustion tube. Close the tube and allow the sample to heat for 1 to 2 min., depending upon the size of the particles. Then admit the oxygen, at a rate of 300 to 400 ml. per min. while combustion is going on. When combustion is complete, slow the current so that the gases leave the absorbents at the rate of about 150 ml. per min. for 6 to 8 min. in order to sweep out the carbon dioxide. Withdraw the absorption tube filled with oxygen, place it in the balance case for 10 min.,[8] open momentarily, and weigh against a similar tube used as a counterpoise. The increase in weight represents carbon dioxide. Multiply this by 27.27 and divide by the weight of the sample to obtain the percentage of carbon in the steel. Remove the boat from the tube and examine the melt for evidences of incomplete combustion. If the drillings are not thoroughly fused in a solid pig, the determination shall be rejected. The proper correction for a blank run on every material used in the determination, except the sample, shall be determined with special care in umpire analyses, or in analyses of very low-carbon material.

High-Sulfur Steels.—Proceed as with carbon steels of low-sulfur content but insert a special SO_2 oxidant in the train such as (1) a tube of platinized silica gel heated to 440° C. and followed by a tube containing ironized asbestos and anhydrone, (2) a tube containing about 25 ml. of an aqueous solution of

[8] The tube will warm up when CO_2 is absorbed. It is not necessary to wait until it reaches room temperature if it is in continuous use, provided the same time interval is maintained, and approximately the same amount of CO_2 is absorbed.

chromic acid (50%), or (3) an aqueous solution of $KMnO_4$ (5%) followed by suitable desiccants.

Alloy Steels.—Proceed as with carbon steels. Although most of the low-alloy steels burn perfectly at 1100° C. without the addition of an accelerator, many alloy steels require an accelerator to obtain complete combustion at this temperature.

If a steel burns with difficulty, either place a small pellet (⅛ in.) of pure tin on each end of the sample (or spread 1 g. of pure tin millings over the sample), or mix with 1 to 2 g. of fine millings of open-hearth iron and proceed as usual.

With high-chromium high-nickel steels (18% chromium, 8% nickel; 20% chromium, 20% nickel, etc.), the principal sources of error in carbon determinations are (1) combustion at too low temperatures and (2) omission of, or faulty corrections for, blank runs. These steels, if burned at the temperatures generally used for carbon determinations (that is, 1050° to 1100° C.), require the aid of an accelerator, such as tin, open-hearth iron, or red lead. More certain combustion of all carbon is obtained if a temperature of 1250° C. or higher is employed and tin or open-hearth iron is used as an accelerator. Preheating is necessary, and burning at higher pressures of oxygen seems advantageous; that is, a sufficiently rapid stream of oxygen should be maintained *during the burning so that it is bubbling freely at the exit end of the train.* After the burning is completed the rate of flow of the oxygen is reduced to about 150 ml. per min. and continued for about 8 to 10 min. If sulfur exceeds 0.06%, proper precautions shall be taken to eliminate oxides of sulfur.

Selenium Steels.—Alloy steels containing selenium evolve volatile selenium oxides during combustion; therefore, a tower packed with asbestos fibers shall be placed in the train between the exit end of the combustion tube and the CO_2 absorbing tube. An aqueous solution of $KMnO_4$ (5%) as used for high-sulfur steels is also satisfactory for this purpose.

Pig, Cast, and Malleable Iron.—Proceed as with carbon steels using a 1-g. sample. Special care shall be used in obtaining a representative sample for the determination of both total carbon and graphite (see Sampling). Precautions for sulfur are of no particular moment for cast irons, except, of course, for continuous combustions of irons of very high sulfur content.

Alloy Cast Irons.—High-silicon and most alloy cast irons require a temperature of at least 1100° C. for complete combustion. Accelerators are desirable for high chromium-nickel irons.

Open-Hearth and Wrought Iron.—Proceed as with carbon steels using a 3- to 4-g. sample and pay special attention to proper blank corrections. With very-low-carbon material, as open-hearth iron, the use of small absorption tubes (Schwartz glass-stoppered, 10 cm., U-shape, containing Ascarite and Anhydrone) tends to reduce errors caused by variations in temperature and humidity.

Graphite in Cast Iron

Special Solutions Required. ***Diluted Nitric Acid (sp.gr. 1.20, approximately).***—Mix 380 ml. of HNO_3 and 620 ml. of water.

Ignited Asbestos.—Gently ignite prepared asbestos under oxidizing conditions until all carbonaceous matter has been consumed. Prepared asbestos is

asbestos (finer than 10-mesh) that has been digested with HCl and then thoroughly washed with water.

Potassium Hydroxide Solution (***sp.gr. 1.10, approximately***).—Dissolve 120 g. of stick KOH in 1000 ml. of water.

Diluted Hydrochloric Acid (***1 : 20***).—Mix 50 ml. of HCl and 1000 ml. of water.

Procedure.—Dissolve 1 to 3 g. of the sample (see Sampling) in 50 ml. of HNO_3 (sp.gr. 1.20) and heat gently on the steam bath, with occasional stirring, until action ceases. If silicic acid separates add 5 ml. of HF to facilitate filtration. Collect the residue, conveniently by suction on ignited asbestos contained in a fused-silica Gooch crucible of such diameter as will fit in the combustion tube. Wash the residue thoroughly with hot water, then with a hot solution of KOH (sp.gr. 1.10), hot water, then with diluted HCl (1 : 20), and finally with hot water. Dry at a temperature not exceeding 150° C., and determine the graphite by direct combustion at approximately 900° C. in the apparatus used for the determination of total carbon, taking care to close the combustion tube immediately after inserting the sample.

MANGANESE BY THE BISMUTHATE METHOD

(Absence of Cobalt)

Special Solutions Required. ***Diluted Nitric Acid*** (***sp.gr. 1.135***).—Mix 280 ml. of HNO_3 with 720 ml. of water.

Diluted Nitric Acid (***3 : 97***).—Boil 40 ml. of HNO_3 under the hood for 1 min., cool somewhat, and pass in a current of purified air for 5 min. Mix 30 ml. of this acid with 970 ml. of water. Add 1 g. $NaBiO_3$, shake, and allow to settle.

Asbestos.—The asbestos for this work shall be shredded, digested with HCl, thoroughly washed with water, then digested on the steam bath with diluted HNO_3 (1 : 3), and finally thoroughly washed with water to remove chlorides and to oxidize any ferrous iron contained in the asbestos. In making the asbestos filter-pad, it is advisable to have a thin, but tight, bed and as much surface as possible. This insures rapid filtration, and the filter may be used until it becomes clogged with bismuthate (about five to six times).

Bismuthate.—The sodium bismuthate shall contain enough active oxygen to correspond to at least 75% $NaBiO_3$. Manganese and chlorides shall not exceed 0.0005 and 0.001%, respectively.

Ferrous Ammonium Sulfate Solution.—Dissolve 12 g. of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a cold mixture of 950 ml. of water and 50 ml. of H_2SO_4.

Standard Potassium Permanganate Solution (***0.03 N, approximately***).—Dissolve 1 g. of $KMnO_4$ in 1000 ml. of water. Let age for one week or more. Filter through purified asbestos. Standardize against the National Bureau of Standards' standard sample 40c of sodium oxalate as follows: Transfer 0.1 g. of the standard sodium oxalate to a 400-ml. beaker. Add 100 ml. of diluted H_2SO_4 (5 : 95) which has been previously boiled for 10 to 15 min. and cooled to 27° ±3° C. Stir until the oxalate has dissolved. Add 40 to 42 ml. of $MKnO_4$ (0.03 N) at a rate of 25 to 35 ml. per min., stirring slowly. Let stand until the pink color disappears. (If the pink color should persist because the permanganate is too strong, discard, and begin again, adding a few milliliters

less of the $KMnO_4$ solution.) Heat to 55° to 60° C. and complete the titration by adding permanganate until a faint pink color persists for 30 sec. Add the last 0.5 to 1 ml. dropwise, with particular care to allow each drop to become decolorized before the next is introduced. Determine the excess of permanganate required to impart a pink color to the solution by matching the color in another beaker containing the same amount of the specially treated diluted H_2SO_4 (5 : 95) at 55 to 60° C.

Standard Sodium Arsenite Solution (0.035 N, approximately).—Dissolve 2 g. of sodium arsenite in water, filter if the solution is not clear, and dilute to 1 liter. The solution is preferably standardized on a standard steel of approximately the same manganese content as the sample. A clear greenish yellow color which does not change when another drop of arsenite is added is a satisfactory end point. As an alternate standardization procedure, 20-ml. portions of the standard solution of $KMnO_4$ (0.03 N) may be titrated in a solution, containing 1 g. of iron as ferric nitrate, under the same condition of acidity and dilution as in the above method. The theoretical titer of the arsenite solution cannot be used because manganese is not quantitatively reduced to the bivalent stage.

Procedure. *Carbon Steel.*—Dissolve 1 g. of the sample in 50 ml. of diluted HNO_3 (sp.gr. 1.135) and boil to expel oxides of nitrogen. Remove from the heat, cool somewhat, add about 0.5 g. of sodium bismuthate, and boil for 2 to 3 min. (With high-carbon steels, about 1 g. of bismuthate, or an amount sufficient to effect either a pink color or a precipitate of MnO_2, should be added.) Clear the solution of permanganic acid or manganese dioxide present by adding a few drops of a saturated solution of SO_2 (freshly prepared) or other suitable reducing agent free from manganese and chlorides, and boil to expel oxides of nitrogen and sulfur. Cool to 15° C. or lower, add 0.5 g. of sodium bismuthate (or an amount equal to 26 times the weight of manganese present) and agitate for 1 min. Add 50 ml. of HNO_3 (3% and free from nitrous acid) and filter through asbestos (or through glass frit or alundum crucibles, sufficiently tight to prevent passage of bismuthate particles). Wash with HNO_3 (3%) until the washings run through colorless. The filtrate must be clear and absolutely free from particles of bismuthate. Titrate by either method (*a*) or (*b*) as follows:

(*a*) *Ferrous Sulfate-Permanganate Titration.*—Treat the filtrate with 2 ml. of phosphoric acid (85%) and then from a burette add enough of the $FeSO_4$ solution to completely discharge (1 to 2 ml. excess) the color of the permanganic acid. Titrate with the permanganate solution to the appearance of a faint pink color. In exactly the same manner carry through a blank determination using the same amounts of acid and bismuthate as was done with the sample. Finally, add the exact volume of ferrous ammonium sulfate solution which was employed and titrate with the standard $KMnO_4$ solution. The difference between the volumes of $KMnO_4$ solution required in the two titrations represents the manganese in the sample.

(*b*) *Arsenite Titration.*—After filtering off the bismuthate, immediately titrate with the arsenite solution to a clear greenish yellow color which does not change upon addition of another drop of arsenite.

Alloy Steels.—Steels containing nickel, molybdenum, and less than 1% of chromium shall be treated like carbon steels, although it is preferable in the

most accurate work to remove chromium if it is present as an essential constituent of the steel (over 0.50% chromium). This may be done by the bicarbonate separation described for chromium-vanadium steels in the next paragraph. An alternative procedure for high chromium alloys consists in dissolving the alloy in HCl-HNO_3 (1 : 1) (or $HClO_4$), adding 20 ml. of $HClO_4$, fuming strongly for 10 min. after the appearance of the red color to oxidize chromium, diluting, precipitating iron and manganese by NH_4OH-$(NH_4)_2S_2O_8$, filtering, and washing. The washed precipitate is then dissolved in 50 ml. of diluted HNO_3 (sp.gr. 1.135) and treated as with carbon steels.

Chromium-Vanadium, Stainless, and Similar Steels.—Dissolve 1 g. of the sample contained in a 300-ml. covered Erlenmeyer flask in 20 ml. of diluted H_2SO_4 (1 : 9). When action is complete, dilute to 100 ml. with boiling water. Add from a burette sodium bicarbonate solution (8%) until a permanent precipitate is formed (approximately 36 ml.) and then 4 ml. more. For high chromium (18%) steel use a 6-ml. excess. Cover the flask, boil for 1 min., and let the precipitate settle. Filter rapidly, conveniently through a cone and paper containing a little paper pulp, and wash the flask and precipitate four or five times with hot water.[9] If the precipitation has been properly performed there will be no more precipitate than can be conveniently handled on an 11-cm. paper. The filtrate will become cloudy in the funnel stem and in the receiving vessel, owing to oxidation and hydrolysis. Heat the filtrate to boiling and oxidize with small portions of HNO_3, adding a total of 12 ml. Evaporate to about 25 ml. Add about 0.5 g. of sodium bismuthate and boil 2 to 3 min. Clear the solution by adding a suitable reducing agent, boil and complete the determination as with carbon steels.[10]

Cast Iron.—Transfer 1 g. of the sample to a small Erlenmeyer flask, add 25 ml. of diluted HNO_3 (1 : 3), heat, and boil 2 to 3 min. after action ceases. Cool, filter and wash the flask and paper with 25 ml. of diluted HNO_3 (1 : 3).

[9] The bicarbonate precipitate does not ordinarily contain more than small amounts (about 0.005%) of manganese. In very accurate work this should be recovered by transferring the precipitate to a beaker, dissolving it in aqua regia, fuming with sulfuric acid, and then carefully adding sodium peroxide in excess and boiling. Chromium and vanadium are thus separated from manganese and iron, which should be filtered off, dissolved in 5 ml. of HNO_3 (1 : 1) and added to the filtrate from the bicarbonate precipitation. A drop of sulfurous acid added to the nitric acid aids in the solution of the manganese dioxide.

[10] Alternately the zinc oxide separation of chromium and manganese may be used in place of the bicarbonate method. The procedure is as follows: Transfer 1 g. of the sample to a 400-ml. beaker, add 25 ml. of diluted HNO_3 (sp.gr. 1.135) and heat gently. If the alloy is not attacked by HNO_3 dissolve in 25 ml. of diluted H_2SO_4 (1 : 5) and oxidize with a few milliliters of HNO_3. When the sample is dissolved, dilute to 200 ml., nearly neutralize with NH_4OH and then add 5-ml. portions of a freshly prepared suspension of ZnO (prepared by thoroughly shaking 50 g. of the finely powdered reagent with 300-ml. of water) until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant. When sufficient ZnO has been added, further addition of the reagent causes the brown precipitate to appear lighter in color. A sufficient excess of ZnO is also indicated by a slightly white and milky supernatant liquid. Allow the precipitate to settle, filter through a rapid filter paper, and wash well with cold water. The ZnO precipitate will retain small amounts of manganese (about 0.005%). Add 12 ml. of HNO_3, and evaporate to about 30 ml. Add about 0.5 g. of sodium bismuthate and boil 2 to 3 min. Clear the solution by adding a suitable reducing agent, boil, and complete the determination as with carbon steels.

Wash the paper a few more times with hot water, and then complete the determination as with carbon steels, including the preliminary oxidation and boiling with bismuthate.

Open-Hearth Iron and Wrought Iron.—Proceed as with carbon steels using 2 to 3 g. of the sample. It is advisable, before filtering the analysis sample, to treat the asbestos pad with a weak solution of $KMnO_4$ and wash it free from the latter with diluted HNO_3 (3%). Very low manganese irons shall not be filtered through pads used previously for higher manganese alloys. Colorimetric determinations by the periodate method on 0.5- to 1-g. samples of open-hearth iron are applicable for routine work.

MANGANESE BY THE PERSULFATE METHOD

(Presence of Cobalt)

Special Solutions Required. ***Acid Mixture.***—Add 100 ml. of H_2SO_4 to 525 ml. of water slowly and with stirring, cool, and add 125 ml. of H_3PO_4 (85%) and 250 ml. of HNO_3.

Silver Nitrate (0.8%).—Dissolve 8 g. of $AgNO_3$ in 1000 ml. of water.

Ammonium Persulfate (25%).—Dissolve 25 g. of $(NH_4)_2S_2O_8$ in 85 ml. of water. The solution must not be kept longer than 12 hr. If the salt is of less than 95% strength, the necessary equivalent must be used.

Standard Sodium Arsenite.—See Bismuthate Method. To standardize, dissolve 1 g. of electrolytic or open-hearth iron of a low and known manganese content (as National Bureau of Standards' standard sample 55*a* of ingot iron) in 30 ml. of the acid mixture. Dilute to 100 ml. with warm water, add exactly 20 ml. of a standard solution of $KMnO_4$ (0.03 N), and then add just enough H_2SO_3 to reduce the $KMnO_4$. Boil for a few minutes to remove oxides of nitrogen. Add 10 ml. of the $AgNO_3$ solution and 10 ml. of the $(NH_4)_2S_2O_8$ solution, boil, cool, and titrate as in the procedure to be described. To obtain the manganese titer, divide the amount of manganese present in the added $KMnO_4$ and open-hearth iron by the milliliters of arsenite required.

Procedure. ***Carbon Steel: 1. Visual Titration.***—Transfer 1 g. of the sample, for a steel containing 1% or less of manganese, or 0.5 g. of the sample, for a steel of higher manganese content, to a 500-ml. Erlenmeyer flask, and add 30 ml. of the acid mixture. Heat until solution is complete, and boil until oxides of nitrogen have been expelled. Add 100 ml. of hot water, 10 ml. of $AgNO_3$ solution and 10 ml. of $(NH_4)_2S_2O_8$ solution. Heat to boiling and *boil briskly* for 1 to 1.5 min. Cool to 30° C. or lower, add 75 ml. of water, and titrate rapidly with standard arsenite solution to a clear yellow end point which does not change upon the addition of more arsenite. If the solution is not titrated rapidly with arsenite, part of the manganese may be reoxidized by the persulfate during the titration and thus yield high results.

2. Potentiometric Titration.—Proceed to the titration stage as in 1, cooling the solution to 15° C. To titrate, bring the needle (or light-beam) on the the solution to 15° C. To titrate, bring the needle (or light-beam) on the scale, and then add the standard arsenite solution. As the end point is approached (rapid fading of the pink color) the needle will remain stationary, or move very slowly. Continue the addition of the arsenite dropwise until a sharp break of four to five divisions is obtained. The potentiometric titration of per-

manganic acid with arsenite is, like the visual, empirical. It is, therefore, necessary to standardize the arsenite solution against a like weight of a standard steel which has approximately the same manganese content as the sample being analyzed and has been treated *exactly* as the latter.

While the potentiometric titration offers no particular advantage over the visual method for steels containing less than 1% of manganese, it is claimed that more reproducible end points can be obtained potentiometrically with steels of high manganese content or in turbid solutions when graphite has not been separated. The apparatus consists essentially of three parts, a motor stirrer, electrodes, and a potentiometric unit. In the Larrabee apparatus the electrodes consist of gold and platinum rods with small vanes at the bottom. In the Kelley apparatus platinum and calomel electrodes are used; it is desirable to insert a salt bridge (Na_2SO_4) solution between the calomel electrode and the titrating solution in this apparatus.

Alloy Steels: Nickel, Chromium-Nickel, Chromium-Vanadium, and Chromium-Vanadium-Molybdenum Steels.—Proceed as with carbon steels.

Chromium Steels (over 4% chromium).—Separate the greater part of the chromium by the bicarbonate separation,[11] using a 6 ml. excess for high chromium (18%) steels. To the filtrate add 30 ml. of the arsenite acid mixture, evaporate to 125 ml. and complete the determination as directed for plain carbon steels. With high carbon (0.8%) high chromium steel, test the bicarbonate precipitate for manganese.[11]

Chromium-Tungsten Steel.—Treat 0.5-g. of the sample with 50 ml. of diluted H_2SO_4 (1 : 9) and 3 ml. of H_3PO_4. Heat until all action ceases. Add 40 ml. of water and 5 ml. of HNO_3, boil until the carbides have dissolved, and proceed as with carbon steels. With chromium-tungsten steels the arsenite solution is preferably standardized on a steel of similar type of known manganese content. Tungsten steels with high carbon (0.8%) and high chromium (4.0%) contents may not be completely decomposed by the H_2SO_4-H_3PO_4 attack. In this case treat the sample with 10 ml. of a mixture of equal parts of HCl and HNO_3 and 4 to 5 drops of HF. When action ceases add 5 ml. of $HClO_4$ (60%) and evaporate just to dryness. Cool, add 5 ml. of H_2SO_4 and fume until $HClO_4$ is expelled. Cool, add 50 ml. of water, 5 ml. of H_3PO_4 (sp.gr. 1.73), dilute to 100 ml. and heat until salts dissolve. If MnO_2 appears, dissolve it with a few drops of H_2SO_3. Complete the determination as with carbon steels.

Cast Iron.—Dissolve as directed for carbon steels, dilute, filter through a rapid paper, wash with hot water, dilute to 125 ml., and complete as with carbon steels.

Open-Hearth Iron.—Proceed as with carbon steels, but use a 2- to 3-g. sample.

Wrought Iron.—Treat 1 g. of the sample as directed for carbon steels.

PHOSPHORUS BY THE MOLYBDATE–MAGNESIA METHOD

Special Solutions Required. ***Diluted Nitric Acid (sp.gr. 1.135).***—Mix 280 ml. of HNO_3 and 720 ml. of water.

[11] See determination of Manganese in Chromium Steels by the Bismuthate Method, p. 1433.

Diluted Nitric Acid (*2 : 100*).—Mix 20 ml. of HNO_3 and 1000 ml. of water.

Potassium Permanganate (*2.5%*).—Dissolve 25 g. of $KMnO_4$ in 1000 ml. of water.

Ammonium Molybdate.—Place in an 800-ml. beaker 65 g. of c.p. ammonium molybdate crystals, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 225 g. of NH_4NO_3, 15 ml. of NH_4OH (sp.gr. 0.90), and 600 ml. of water. Stir and heat gently. When the crystals have dissolved, filter (without washing) and dilute to 1000 ml. with water.

Magnesia Mixture.—Dissolve 65 g. of $MgSO_4$ and 75 g. of $(NH_4)_2SO_4$ in 500 ml. of water. Add NH_4OH in slight excess and let stand overnight; filter if a precipitate appears. Make just acid by adding a very slight excess of H_2SO_4, dilute to 1 liter, and keep in a glass-stoppered bottle.

Diluted Ammonium Hydroxide (*1 : 20*).—Mix 100 ml. of NH_4OH (sp.gr. 0.90) and 2000 ml. of water.

Potassium Nitrate (*1%*).—Dissolve 10 g. of KNO_3 in 1000 ml. of water.

Procedure. ***Carbon Steels.***—Transfer 4 g. of the sample [12] to a 300-ml. Erlenmeyer flask, dissolve the sample in 125 ml. of diluted HNO_3 (sp.gr. 1.135), oxidize the organic matter by adding 10 ml. of the solution of $KMnO_4$ (2.5%) and boil for 3 to 5 min. If no precipitate forms, add more $KMnO_4$ and boil again. Dissolve the precipitate by the dropwise addition of a saturated solution of Na_2SO_3 or H_2SO_3, and boil for a few minutes to expel oxides of nitrogen. Cool to about 75° C. and add 85 ml. of molybdate reagent. Stopper the flask, shake for 10 min., and allow to stand for 2 hr. or more. Filter through a tight filter paper. Wash the flask, precipitate, and paper with the cold diluted HNO_3 (2 : 100) and then five times with KNO_3 solution.

Set the filtrate and washings aside after thorough mixing, and note whether further separation of phosphomolybdate occurs. Dissolve the precipitate on the filter and in the flask in 20 ml. of diluted NH_4OH (1 : 1) to which has been added 2 g. of citric acid, catch the solution in a 250-ml. beaker, wash the filter several times with diluted NH_4OH (1 : 20), then with hot water, and finally several times with diluted HCl (1 : 20). If the ammoniacal solution of the phosphomolybdate is not clear at this point, heat it to boiling, filter through the same paper, wash the paper with hot water, ignite in a small platinum crucible, and fuse any residue with as little Na_2CO_3 as possible (not over 0.5 g.); extract the cooled melt with hot water, cool, filter, and add the water solution to the ammoniacal solution.

Render the ammoniacal solution acid with HCl, add 20 ml. of the acid magnesia mixture, cool in ice water, and then add NH_4OH slowly until the solution is faintly ammoniacal. Stir vigorously for 5 min. or until a crystalline precipitate appears,[13] and finally add 5 to 10 ml. of NH_4OH. The volume of the solution at this point should not exceed 100 ml. Allow the solution to stand in a cool place for 4 to 6 hr., or, preferably, overnight. Filter and wash the precipitate moderately with diluted NH_4OH (1 : 20). Dissolve the precipitate on the filter in 20 ml. of diluted HCl (1 : 1), catching the solution in the original beaker. Wash the filter thoroughly with warm diluted HCl

[12] If the percentage of phosphorus is less than 0.05%, it is advantageous to treat two or more 4-g. samples as described, and combine the yellow precipitates either by filtering through the same paper or by combining the precipitates after filtering on separate papers.

[13] If the amount of phosphorus is very small, it may take 30 min. to 1 hr. before the precipitate begins to appear.

(1 : 1). Add 0.5 to 1 g. of NH_4Br[14] and gently boil the HCl solution to a volume of 5 to 10 ml. (but not to dryness) to eliminate arsenic. Dilute to a volume of 50 to 75 ml., add 0.1 to 0.2 g. of citric acid, 2 to 3 ml. of the acid magnesia mixture, and cool in ice water. Make ammoniacal, stir as above, and allow to stand in a cool place for 4 to 24 hr.

Filter, wash with diluted NH_4OH (1 : 20), and ignite the precipitate carefully and at as *low a temperature* as possible until the carbon has been destroyed and the residue is white. Finally, ignite to constant weight at 1000 to 1100° C. Dissolve the ignited precipitate in 5 ml. of diluted HNO_3 (1 : 1) and 20 ml. of water. If no residue remains, the ignited precipitate may be regarded as $Mg_2P_2O_7$. If a residue remains, filter, wash with hot water, ignite, and weigh. Treat with a few drops of HF, evaporate to dryness, ignite, and reweigh. Subtract any loss of weight from the original weight of the pyrophosphate, and calculate the percentage of phosphorus on the basis of this purified magnesium pyrophosphate.

Alloy Steels: Nickel, Chromium-Nickel, Stainless and Similar Alloy Steels Containing Neither Tungsten nor Vanadium.—Proceed as with carbon steels. High-chromium steels (stainless), high-chromium high-nickel (18% chromium, 8% nickel; 20% chromium, 20% nickel), and other steels in this group that do not dissolve in diluted HNO_3 (sp.gr. 1.135), shall be treated as follows: Treat 3 g. of the sample in a 500-ml. Erlenmeyer flask with 75 ml. of a mixture of equal parts of HCl and HNO_3, and heat gently. When decomposition is complete, add 25 ml. of $HClO_4$ (60%) and evaporate until fumes of $HClO_4$ are evolved. Continue the heating for 5 min. to oxidize chromium and to dehydrate silica. Cool somewhat, add 40 ml. of water, filter, and wash the flask, paper, and silica with 55 ml. of diluted HNO_3 (sp.gr. 1.2). Add $KMnO_4$ to the filtrate, boil, add H_2SO_3 to destroy oxides of manganese and to reduce all of the chromium, and proceed as usual. As an alternative method, the sample may be decomposed by heating with diluted HNO_3 (1 : 1) and adding small portions of either HF or HCl.

Austenitic Manganese Steels (over 10% manganese).—Transfer 4 g. of the sample to a 300-ml. Erlenmeyer flask, add 70 ml. of diluted HNO_3 (sp.gr. 1.135) and digest until action ceases. Add 35 ml. of $HClO_4$ (60%) and evaporate just to fumes. Add HF dropwise until all of the silica is in solution and then an excess of 5 drops. Fume so that the $HClO_4$ refluxes on the sides of the flask for 25 to 30 min. Cool, add 50 ml. of water and 10 ml. of HNO_3. Add a few drops of $KMnO_4$ (2%) and boil until oxides of manganese are precipitated. Dissolve the precipitated manganese with H_2SO_3 and boil a few minutes to expel oxides of nitrogen. Cool to 70° C. and precipitate with molybdate, etc., as with carbon steels.

Chromium-Vanadium Steels or Other Steels Containing Vanadium but No Tungsten.—Proceed as with carbon steels until the solution is ready for the addition of the molybdate reagent. At this point cool to 10° C., add 5 ml. of a solution of ferrous sulfate (100 g. of $FeSO_4 \cdot 7H_2O$, in 1000 ml. of diluted H_2SO_4 (5 : 95)) and 2 to 3 drops of H_2SO_3. Mix, add 85 ml. of molybdate, shake for 10 min., and allow to stand for 4 hrs. or, preferably, overnight. Filter, and finish the determination as directed for carbon steels.

[14] With a precipitation temperature of 25° C., arsenic, when present in small amounts, is not precipitated, and therefore the HBr treatment can be omitted.

High-Speed Steels or Other Steels Containing Tungsten and Vanadium.—Decompose 4 g. of the sample in 125 ml. of diluted HNO_3 (sp.gr. 1.135), add 30 ml. of HCl and evaporate to dryness. Take up the residue in 20 ml. of diluted HCl (1 : 1), dilute to 100 ml. with hot water, and filter off the tungstic acid.[15] Evaporate the filtrate twice with 20-ml. portions of HNO_3 to expel the HCl, taking the second evaporation just to a syrup; add 65 ml. of diluted HNO_3 (sp.gr. 1.135), and filter the solution if it is not entirely clear. Cool to 10° C., add 5 ml. of a solution of $FeSO_4$ (100 g. in 1000 ml. of diluted H_2SO_4 (5 : 95)) and 2 to 3 drops of H_2SO_3. Mix, add 85 ml. of molybdate reagent, shake for 10 min., allow to stand for 4 hrs., or preferably, overnight. Filter and finish the determination as directed for carbon steels.

Cast Iron.—Dissolve 2 to 3 g of the sample in a covered casserole in 30 ml. of diluted HNO_3 (1 : 1). When solution is complete, add 10 ml. of diluted HCl (1 : 1), evaporate to dryness, and bake for 15 to 20 min. on the hot plate. Cool, drench the residue with HCl, dilute to 50 ml. with hot water, and warm until the salts are in solution. Filter without delay, wash with diluted HCl (1 : 20), and evaporate the filtrate to syrupy consistency. In the meantime, place the paper containing the graphite and silica in a platinum crucible, burn the carbon in a good oxidizing atmosphere, cool, and add 5 to 10 drops of HCl and 1 to 2 ml. of HF. Evaporate just to dryness, take up any residue [16] in 5 ml. of HCl, and add the solution to the main solution which is being evaporated. When the solution is of syrupy consistency, transfer it to a 300-ml. Erlenmeyer flask by alternate washing with diluted HNO_3 (1 : 1) and hot water, using not more than 30 ml. of the former and 70 ml. of the latter. Nearly neutralize with NH_4OH, and add 100 ml. of molybdate reagent. Shake for 10 min. and allow to stand for 4 to 6 hrs., or preferably, overnight. Complete the determination as with carbon steels.

Open-Hearth Iron and Wrought Iron.—Proceed as with carbon steels.

PHOSPHORUS BY THE ALKALIMETRIC METHOD

Special Solutions Required.—In addition to those listed under the molybdate-magnesia method, the following special solutions will be required:

Standard Sodium Hydroxide.—Transfer 6.5 g. of C.P. NaOH to a 1-liter flask. Add 1000 ml. of water, and a slight excess of a solution of $Ba(OH)_2$.

[15] This precipitate may contain a small amount of phosphorus, and in standardization work it shall be treated as follows: Transfer the bulk of the precipitate to an Erlenmeyer flask with a jet of water, and then treat the paper with 25 ml. of hot diluted NH_4OH (1 : 4) containing 0.5 g. of citric acid. Catch the filtrate in the flask containing the remainder of the precipitate. Wash the paper with hot water, then a few times with hot diluted HCl (1 : 20), holding the volume of the filtrate and washings to about 75 ml. Slightly acidify the solution with HCl, add 25 ml. of the acid magnesia mixture and about 10 ml. of NH_4OH in excess. Add a few glass beads, cool the solution in ice water, stopper the flask, and shake thoroughly for 1 hr. Allow to stand overnight at about 0° C. Filter, and wash a few times with diluted NH_4OH (1 : 20). Dissolve the precipitate in a little hot diluted HNO_3, and add it to the original solution in which phosphorus is to be determined, or determine the phosphorus separately by precipitating it with molybdate reagent and titrating with standard alkali and acid. This recovery usually amounts to less than 0.001% and need not be made in routine analyses.

[16] If the percentage of titanium or zirconium is high, this residue should be fused with Na_2CO_3, extracted with hot water, cooled, filtered, and the water extract added to the main solution.

Stopper and let stand for 24 hrs. Decant the liquid, and standardize it against a steel of known phosphorus content, as determined by the molybdate-magnesia method. Appropriate National Bureau of Standards' standard steels are recommended for this purpose. The solution may also be standardized by use of the National Bureau of Standards' standard sample 84 of acid potassium phthalate and the ratio 23 NaOH to 1 phosphorus. Protect the alkali solution from carbon dioxide by means of a soda-lime or soda-asbestos tube.

Standard Nitric Acid.—Mix 7 ml. of clear HNO_3 with 1 liter of water and standardize against the standard alkali solution, using phenolphthalein as the indicator. If desired, the acid solution may be rendered equivalent to the NaOH by dilution with water.

Phenolphthalein Indicator.—Dissolve 0.29 g. of reagent in 100 ml. of ethyl alcohol (50%).

Procedure. ***Carbon Steels.***—Transfer 2 to 3 g. of the sample to a 300-ml. Erlenmeyer flask, dissolve [17] the sample in 65 ml. of diluted HNO_3 (sp.gr. 1.135) and oxidize organic matter by adding 10 ml. of the $KMnO_4$ (2.5%) and boiling for 2 to 3 min. If no precipitate forms, add more $KMnO_4$ and boil again. Dissolve the precipitate by the dropwise addition of a saturated solution of Na_2SO_3 or H_2SO_3 and boil for a few minutes to expel oxides of nitrogen. Adjust the volume to 60 ml. and the temperature to 45° C., and add 50 ml. of the molybdate reagent. Stopper the flask, shake for 10 min., and allow the precipitate to settle. Filter through a 9-cm. close-texture paper. Wash the flask, precipitate, and paper twice with 5-ml. portions of diluted HNO_3 (2 : 100) and then five times with 5-ml. portions of a solution of KNO_3 (1%). Finally, wash the paper about ten times (until free from acid), directing the jet of KNO_3 solution around the edge of the paper and then spirally down. Return the paper and precipitate to the flask, add 25 ml. of water and a 2- to 5-ml. excess of standard NaOH, both free from carbon dioxide, and shake or stir until the precipitate is dissolved. Dilute to about 150 ml. with water free from carbon dioxide, add 3 drops of the phenolphthalein indicator, and discharge the pink color with standard HNO_3.

Alloy Steels: Nickel, Chromium-Nickel, Stainless, and Similar Alloy Steels Containing Neither Tungsten nor Vanadium.—Proceed as with carbon steels. With high-chromium nickel, or other steels insoluble in diluted HNO_3, treat 2 g. of the sample with 50 ml. of a mixture of equal parts of HNO_3 and HCl, add 4 to 5 drops of HF, heat till action ceases and then add 20 ml. of $HClO_4$. Evaporate to fumes, fume 5 to 10 min., filter, etc. (as in the molybdate-magnesia method),[18] and finish by the alkalimetric method. With steels of appreciable titanium content (over 0.25% titanium) it is best to remove titanium before precipitating the phosphomolybdate.

Austenitic Manganese Steel (***greater than 10% manganese***).—Transfer 2 g. of the sample to a 400-ml. beaker, add 35 ml. of diluted HNO_3 (sp.gr. 1.135) and digest until action ceases. Add 20 ml. of $HClO_4$ (60%) and evaporate just to fumes. Add HF dropwise until all of the silica is dissolved and then add an excess of 5 drops. Fume so that $HClO_4$ refluxes on the sides of the beaker for 20 to 25 min. Cool, add 50 ml. of water and 10 ml. of HNO_3. Add

[17] To prevent the possibility of silica precipitating in steel of high silicon content, *3 to 4 drops* of HF may be added while the sample is dissolving.

[18] See p. 1437.

a few drops of $KMnO_4$ (2%) and boil until oxides of manganese are precipitated. Dissolve the precipitated manganese with H_2SO_3 and boil for a few minutes to expel oxides of nitrogen. Transfer the solution to a 300-ml. Erlenmeyer flask and adjust the volume to 60 ml. and the temperature to 45° C.[19] Add 50 ml. of ammoniacal molybdate solution, shake 10 min. and let stand for 20 min. Filter, wash, and titrate as directed for carbon steels.

Chromium-Vanadium Steel, or Other Steels Containing Vanadium but No Tungsten.—Proceed as with carbon steels until the solution is ready for the addition of molybdate reagent. At this point cool to 10° C., add 5 ml. of a solution of ferrous sulfate (100 g. $FeSO_4 \cdot 7H_2O$ in 1000 ml. of diluted H_2SO_4 (5 : 95)) and 2 to 3 drops of H_2SO_3. Mix, and then add 50 ml. of molybdate reagent. Shake for 10 min., allow to settle 1 hr., filter, and finish as directed for carbon steel.

High-Speed Steels, or Other Steels Containing Tungsten and Vanadium.—For the decomposition of the sample (2 g.) and the preparation of the solution for the precipitation of the ammonium phosphomolybdate proceed as in the gravimetric method for the determination of phosphorus in these steels.[2c] Precipitate the phosphorus in a cool reduced solution and finish the determination as described for chromium-vanadium steels by the alkalimetric method (see preceding paragraph).

Cast Iron.—Dissolve 0.5 to 2 g. of the sample in 65 ml. of diluted HNO_3 (sp.gr. 1.135). Filter through a paper of loose texture and catch the filtrate in a 300-ml. Erlenmeyer flask. Wash the paper a few times with diluted HNO_3 (2 : 100) and then with about 50 ml. of hot water.[21] Add 10 ml. of $KMnO_4$ to the filtrate and boil for 3 to 5 min. Dissolve the precipitated oxides by the dropwise addition of a saturated solution of Na_2SO_3 or H_2SO_3 and boil for a few minutes to expel oxides of nitrogen. Cool to 45° C., add 50 ml. of molybdate reagent and proceed as with carbon steels.

Open-Hearth Iron.—Proceed as with carbon steels. The result shall be corrected by that obtained in a blank run.

Wrought Iron.—Proceed as with carbon steels using 1 g. of the sample. In wrought iron phosphorus will be present as phosphide and as phosphate (in slag inclusions). If a differentiation between the two forms is desired, determine total phosphorus in one sample; determine the phosphate that is left after phosphine has been driven off (by attack with a non-oxidizing acid as HCl) from another sample, and the phosphorus occurring as phosphide is then obtained by difference. The accuracy of the results obtained by this phosphate-phosphide method is somewhat doubtful, but the method is apparently the only one available at present.

SULFUR BY THE GRAVIMETRIC METHOD

Special Solutions Required. ***Barium Chloride Solution (10%).***—Dissolve 100 g. of $BaCl_2 \cdot 2H_2O$ in 1000 ml. of water.

[19] If the solution at thin point contains silica, filter, wash with water, boil until the volume of the filtrate is approximately 60 ml., and again cool to 45° C.

[20] See p. 1438.

[21] For treatment of the residue when the iron contains appreciable amounts of titanium or zirconium see the Determination of Phosphorous in Cast Iron by the Molybdate-Magnesia Method, p. 1438.

Diluted Hydrochloric Acid (1 : 99).—Mix 10 ml. of HCl (sp.gr. 1.19) and 990 ml. of water.

Procedure. Carbon Steel.—Dissolve 4.57 g. of the sample in 50 ml. of HNO_3 [22] in a covered beaker or flask. In case solution is slow or difficult, HCl may be added dropwise at intervals. With steels that dissolve too rapidly, it is necessary to place the cooled acid in a covered beaker and add the sample in small portions. When solution is complete, add 0.5 g. of Na_2CO_3 and carefully evaporate to low volume (about 10 ml.)[23] in a sulfur-free atmosphere. Cool, add 30 ml. of HCl, and evaporate just to dryness. Add 30 ml. more of HCl, and evaporate to syrupy consistency.[24] Add 10 ml. of HCl, 25 ml. of water, 5 g. of 20- to 30-mesh zinc (free from sulfur), and warm on the steam bath until the iron is reduced to the ferrous state and the evolution of hydrogen has nearly ceased. Remove the silica and undissolved zinc by filtration through a tight filter paper, wash with approximately 75 ml. of diluted HCl (1% by volume), warm to 60° to 70° C. and add 10 ml. of the solution of $BaCl_2$ (10%).[25] Stir vigorously and let stand 18 to 24 hrs. Filter on a 9-cm. paper of close texture and discard the filtrate. Wash once or twice with cold diluted HCl (1 : 500) and then with hot water until free from chlorides. Reserve the precipitate and evaporate the washings to dryness. Dissolve the slight residue in 1 ml. of diluted HCl (1 : 1), dilute to 25 ml. with hot water, add 1 ml. of $BaCl_2$ (10%), and digest at 70° to 80° C. for several hours, avoiding any undue loss by evaporation. Filter on a small paper of close texture and wash with hot water until free from chlorides.[26] Ignite both papers in platinum and treat with one drop of H_2SO_4 (1 : 1) and 1 ml. of HF. Evaporate to dryness, ignite, and weigh. Duplicate blanks shall be carried through all steps of the determination. The corrected weight of the ignited $BaSO_4$ multiplied by three is equal to the percentage of sulfur.

Alloy Steels.—For steels which can be dissolved in HNO_3, or HNO_3 plus small portions of HCl, proceed as with carbon steels. High chromium-nickel steels shall be dissolved in a 400-ml. tall-form beaker in 150 ml. of a mixture of equal parts of HNO_3 and HCl. The acids shall first be thoroughly mixed in another container and, when thoroughly red, added to the beaker containing the sample. If the reaction proceeds too rapidly the beaker and contents should be chilled by placing them in ice water.

Alternately, the following Meineke method (solution in acid copper potassium chloride) may be used for the chromium-nickel alloys.

Meineke Method.—Dissolve the sample (4.57 g.) in 250 ml. of copper potassium chloride solution (dissolve 300 g. of 2 $KCl \cdot CuCl_2 \cdot 2H_2O$ in a mixture

[22] The addition of 2 to 5 ml. of bromine is claimed to effect more complete recovery of sulfur.

[23] The use of a coarse screen of ⅛ in. wire, triangles, or an asbestos pad on the hot plate permits of more rapid evaporation without the danger of spattering.

[24] The HNO_3 can also be expelled by adding about 50 ml. of $HClO_4$, evaporating to fumes of $HClO_4$, and fuming for about 5 min. The solution is then cooled, diluted to 75 ml., reduced with zinc, filtered, $BaCl_2$ added, and the procedure continued as described.

[25] The solution should preferably contain not more than 2% by volume of HCl at the time of the precipitation with $BaCl_2$. Ordinarily, there will be no hydrolysis of iron during the filtration and washing of the undissolved zinc or the precipitation with $BaCl_2$. Should this occur, the solution must be cleared by the addition of HCl, having due regard to the final permissible acidity.

[26] This recovery of $BaSO_4$ ordinarily represents from 0.001 to 0.003% sulfur.

of 1000 ml. of water and 75 ml. of HCl) at room temperature and with mechanical stirring (slow).[27] Filter through purified asbestos. Wash two or three times with diluted HCl (2 : 98). Return the residue and asbestos pad to the beaker and treat with 20 ml. of HNO_3. Heat and add $KClO_3$ until all carbonaceous matter is destroyed. Graphite may be ignored. Evaporate the solution to dryness, take up in 10 ml. of HCl and again evaporate to dryness. Take up in 10 ml. of diluted HCl (1 : 9) and 20 ml. of water, filter through paper and wash with 50 ml. of hot water. Boil and add 5 ml. of $BaCl_2$ (10%). Digest for about 2 hrs., filter, and finish the determination as directed in the HNO_3 method (see preceding paragraph).

Tungsten Steels.—Transfer 4.57 g. of the sample to a 600-ml. beaker or Erlenmeyer flask and treat with 75 ml. of HNO_3. If reaction is slow, heat gently; if it is vigorous, cool in ice water. If reaction is very slow, add 5 ml. of HCl or a drop or two of HF occasionally as the solution is heated on the steam bath.[28] When HNO_3 alone is used, the particles of steel tend to become covered with a film of tungstic acid. Stirring or rubbing these coated granules speeds up the decomposition. When reaction is complete, digest until the residue is pure yellow and contains no dark material, adding fresh portions of acid if necessary. Evaporate to syrupy consistency. Cool, add 30 ml. of HCl, and again evaporate to syrupy consistency. Add 100 ml. of hot water and boil until soluble salts are in solution. Filter and wash the residue with diluted HCl (1 : 10), catching the filtrate and washings in a 600-ml. casserole. Evaporate to dryness, add 30 ml. of HCl, and again evaporate to dryness. Cool, add 60 ml. of diluted HCl (1 : 1), warm until salts are in solution, and add 50 ml. of boiling water. Add 10 ml. of cinchonine solution (125 g. of cinchonine dissolved in 1000 ml. of diluted HCl (1 : 1)), and let stand overnight. Filter and wash with cinchonine wash water (30 ml. of cinchonine solution diluted to 1000 ml.). Evaporate the filtrate and washings until a slight film begins to form and proceed with the reduction by zinc as with carbon steels. In this determination it is particularly important that corrections be made as determined by blanks carried through all steps of the method. As cinchonine sometimes contains sulfur, this solution should be measured so that the same amount is used in the blank as in the determination. If the cinchonine contains excessive quantities of sulfates, wash the crystals on a Büchner funnel with water until the washings no longer give a precipitate with barium chloride.

Open-Hearth Iron.—Proceed as with carbon steels.

Cast Iron.—Proceed as with carbon steels.

Wrought Iron.—Proceed as with carbon steels.

SULFUR BY THE EVOLUTION METHOD

Apparatus.—Figure 185 shows a typical apparatus for this determination.

Special Solutions Required. ***Diluted Hydrochloric Acid (1 : 1).***—Mix 500 ml. of HCl and 500 ml. of water.

Ammoniacal Zinc Sulfate.—Dissolve 200 g. of $ZnSO_4 \cdot 7H_2O$ in 1000 ml. of water, and add 1000 ml. of NH_4OH (sp.gr. 0.90). Let stand 24 hrs. and filter.

[27] Selenium is also obtained with sulfur in the residue, hence with selenium steels, all operations should be conducted under a good hood.

[28] Alternately, the sample may be treated with 150 ml. of a mixture of HCl and HNO_3 as in alloy steels.

Ammoniacal Cadmium Chloride.—Dissolve 10 g. of $CdCl_2$ in 400 ml. of water and add 600 ml. of NH_4OH (sp.gr. 0.90).

Starch Solution.—To 500 ml. of boiling water, add a cold suspension of 5 g. of soluble (or arrowroot) starch in 25 ml. of water, cool, add a cool solution of 5 g. of NaOH in 50 ml. of water; then add 15 g. of KI and mix thoroughly.

Potassium Iodate.—Dissolve 1.12 g. of KIO_3 and 12 g. of KI in 1000 ml. of water. For general work the theoretical sulfur titer of this solution shall be used; for specialized work on one kind of material, the solution may be standardized against like material. The theoretical titer is based on standard sodium oxalate and is obtained as follows: To 300 ml. of water in a 600-ml. flask, preferably glass-stoppered, add 10 ml. of HCl (sp.gr. 1.19) and 1 g. of KI. Cool and add 25 ml. of $KMnO_4$ (0.03 N) which has been standardized against sodium oxalate. Swirl gently, stopper, and let stand for 5 min. Titrate the liberated iodine with thiosulfate solution (approximately 0.03 N) until the color nearly fades. Then add 5 ml. of starch solution and continue the titration until the blue color is just destroyed. In a new flask, repeat the experiment with the sole difference that 25 ml. of the iodate solution is substituted for the standard permanganate solution. Calculate the normality of the iodate solution, and dilute it if desired so that its normality is 0.0312, or 1 ml. is equivalent to 0.01% of sulfur on a 5-g. sample. For standardization against like materials, 5-g. portions of the proper standard are carried through all steps of the method. The following equations represent the reactions that are involved:

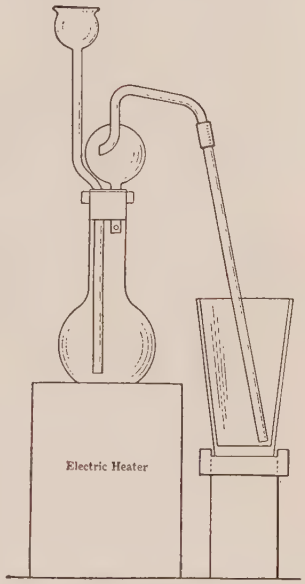


FIG. 185.—Apparatus for Determination of Sulfur by the Evolution Method.

$$2KMnO_4+10KI+16HCl\rightarrow 5I_2+12KCl+2MnCl_2+8H_2O$$
$$KIO_3+5KI+6HCl\rightarrow 3I_2+6KCl+3H_2O$$
$$I_2+2Na_2S_2O_3\rightarrow Na_2S_4O_6+2NaI$$

The normality of the iodate solution is then found by dividing the volume of $Na_2S_2O_3$ solution required in the second titration by the volume required in the first, and multiplying by the normality factor of the solution of $KMnO_4$. If the solution is then diluted so that the normality is 0.0312, 1 ml. represents 0.01% of sulfur on a 5-g. sample.

Procedure. *Carbon Steel.*—Place 5 g. of the sample in the dry flask and connect the latter as shown in Fig. 185. Place 10 ml. of the ammoniacal solution of zinc sulfate or cadmium chloride and 150 ml. of water in the tumbler. Add 80 ml. of the diluted HCl (1 : 1) to the flask through the thistle tube, heat the flask and its contents gently until the solution of the iron is complete, then boil the solution for 30 sec. The heat shall be so adjusted that there is a rapid, steady evolution of gas. Disconnect the delivery tube, leaving it in the solu-

tion, and remove the tumbler. Add 2 ml. of starch solution, then 40 ml. of diluted HCl (1 : 1) and titrate immediately with the iodate solution to a permanent blue color.

NOTES.—Direct sunlight must be avoided if cadmium solutions are used, otherwise low results are obtained.

This method succeeds best when the evolution of gas is rapid and the conditions are kept constant.

Trouble may occur if the absorbing solution becomes too hot. This condition can be avoided by keeping the absorbing solution in a water bath.

Some analysts prefer to add the diluted HCl at a temperature of 80° to 90° C. and to heat the flask on an electric heater instead of over gas. The use of concentrated HCl necessitates a condensing arrangement and does not offer any general advantages over the diluted acid for carbon steel.

With most carbon steels, the results for sulfur which are obtained by the evolution method and the use of the theoretical sulfur titer check the gravimetric results within ±0.002%. Some steels dissolve too slowly and some (for example, certain steels containing high sulfur or high carbon) do not yield all of their sulfur. In such cases the samples must be annealed as follows: Place 5 g. of the sample in a 20-ml. porcelain crucible. Cover with a ¼-in. layer of graphite, Acheson No. 38, cover the crucible and heat at 685° C. for 20 min. Transfer the cooled annealed steel and graphite to the evolution flask and proceed as in the regular method.

Alloy Steels.—Many alloy steels yield all their sulfur when analyzed by the same procedure as is used for carbon steels, but some yield only a part. Hydrochloric acid of 2 : 1 strength, or the concentrated acid (sp.gr. 1.19) with some alloy steels, will give slightly more evolved sulfur than does the 1 : 1 acid. For example, some molybdenum steels yield most of their sulfur with concentrated HCl. For high silicon steels, concentrated HCl plus a small amount of HF (0.5 ml.) has been recommended. The evolution method, however, can be used only if experiment has shown that all sulfur is evolved as H_2S in the particular type of steel under analysis. The evolution method is not satisfactory for the determination of sulfur in selenium steels.

Cast Iron.—Most cast irons do not give up all their sulfur as hydrogen sulfide. The amount that is given off can often be increased by annealing the sample, although with many irons annealing yields no increase in the amount of evolved sulfur. Annealing is done as directed in the second preceding paragraph.

With high-silicon cast irons, use hot (70° C.) diluted HCl (1 : 1), heat rapidly to boiling, and then simmer. If the solution froths badly, add about 0.5 ml. of HF.

Concentrated HCl has been recommended for certain alloy cast irons, in which case suitable condensing arrangements must be provided. Even then care must be taken to avoid excessive neutralization of the alkaline absorbent.

Open-Hearth Iron and Wrought Iron.—Proceed as with carbon steels.

SILICON BY THE SULFURIC ACID METHOD

Procedure. Carbon Steels.—Transfer the sample (4.672 g. if silicon is under 0.5%, and 2.336 g. if it is over this percentage) to a 300-ml. casserole,

treat with 100 ml. of diluted H_2SO_4 (1 : 4), and cover.[29] Warm gently. When reaction ceases, remove and rinse the cover, and evaporate the solution, taking care to avoid spattering, until copious fumes of H_2SO_4 are given off. Replace the cover and continue the fuming for 2 to 3 min., but no longer since insoluble sulfates may be formed. Cool somewhat, and add 100 ml. of warm water (40° to 50° C.) at one time. Stir until salts are in solution, heating gently if necessary but never boiling. Filter immediately using a rapid ashless filter paper for high-silicon steels, and a tighter paper for low-silicon steels. Transfer all the residue to the paper, scrubbing the casserole thoroughly with a rubber-tipped rod. Wash the paper and residue alternately with hot diluted HCl (5 : 95) and hot water until salts of iron have been removed. This usually requires six washings with 5-ml. portions of each solution. Transfer the paper and residue to a platinum crucible, heat carefully until the carbon is gone, and then cover and ignite for 10 to 15 min. at 1050° to 1100° C. Cool in a desiccator and weigh. Add enough diluted H_2SO_4 (1 : 1) to moisten the SiO_2 and then 3 to 5 ml. of HF. Evaporate to dryness, carefully heat until H_2SO_4 is gone, and then ignite at 1000° C. Cool in a desiccator and weigh. If the factor weight was taken the loss in weight multiplied by 10 represents the percentage of silicon.

NOTE.—In the above and succeeding methods some silica passes into the filtrate. The amount left in solution depends chiefly on the silicon content of the alloy, that is, about 0.005% silicon for a 0.1% silicon steel, approximately 0.02% for a 0.4% silicon steel and about 0.05% or more for a 4.5% silicon steel. Hence in umpire work it is necessary to evaporate the filtrate and washings to fumes of H_2SO_4, dilute, filter, and ignite the washed paper and contents with the first portion.

Alloy Steels.—Proceed as with carbon steels if the sample dissolves in diluted H_2SO_4. If it does not, use the acid mixture (given for carbon steels) or the perchloric acid method.[30] The latter is especially suited for high-chromium alloys.

Tungsten Steels.—Transfer 2.336 g. of the sample to a beaker or casserole provided with a cover glass. Add a mixture of 20 ml. of HCl and 20 ml. of HNO_3, and warm until all the steel has dissolved. Add 60 ml. of warm diluted H_2SO_4 (1 : 1), and evaporate until copious fumes of H_2SO_4 appear. Cool somewhat, cautiously add 5 ml. of HCl, and swirl gently until well mixed. Add 125 ml. of warm water (40° to 50° C.), and proceed as in the sulfuric acid method. Ignite the tungstic acid and silica together at a temperature of about 1000° C. and weigh. Treat with HF and H_2SO_4, ignite at 800° C., and again weigh.

Cast Iron.—Proceed as with carbon steel, using 2.336-g. of the sample. With gray or mottled pig iron it is desirable to use a finely divided sample and to boil vigorously with slightly more acid at the start, as the particles tend to become coated with gelatinous silica.

[29] More rapid and equally satisfactory determinations can be made by dissolving the sample in 40 ml. of diluted HCl (1 : 1), evaporating to low volume, then adding the H_2SO_4 and evaporating to fumes, etc. Another alternate procedure consists in dissolving the sample in 80 ml. of an acid mixture (600 ml. of water, 200 ml. of H_2SO_4 (sp.gr. 1.84), 100 ml. of HNO_3 (sp.gr. 1.42) and 100 ml. of HCl (sp.gr. 1.19)), heating until solution is complete, and then evaporating to copious fumes of H_2SO_4, etc. In this method 5 ml. of HCl is added to the partially cooled residue before dilution with warm water.

[30] See p. 1446.

Open-Hearth Iron.—Proceed as with carbon steels using 10- to 20-g. samples and corresponding amounts of H_2SO_4. Fume gently for 12 to 15 min. instead of 1 to 2 min. as with carbon steels. Umpire analyses of open-hearth iron must be made in platinum dishes.

Wrought Iron.—Dissolve 4.672 g. of the sample in 80 ml. of the acid mixture (as given for carbon steels), evaporate, and fume for 1 to 2 min. Cool somewhat and cautiously add to the warm solution 5 ml. of HCl as the solution is swirled gently. When well mixed, add 125 ml. of warm water, stir, and complete the determination as directed for carbon steels.

SILICON BY THE PERCHLORIC ACID METHOD

Procedure. *Carbon Steels.*—Transfer 4.672 g. of the sample for steels containing less than 0.5% silicon and 2.336 g. for steels containing more than 0.5% silicon to a 400-ml. beaker. Add 40 ml. of HNO_3 (sp.gr. 1.20).[31] Heat cautiously until solution is complete. Then raise the cover and add 40 ml. of $HClO_4$ (60 to 70%) for the 2.3-g. sample, or 60 ml. for the 4.7-g. sample. Evaporate to fumes, cover the beaker, and continue to heat at such a rate that $HClO_4$ refluxes on the sides of the beaker for 15 to 20 min. Cool somewhat, add 125 ml. of hot water, stir until salts are in solution, crushing up any lumps of silica with a flattened rod. Filter immediately and proceed as in the sulfuric acid method. The washing of the paper must be thorough, for residual $HClO_4$ held in the silicic acid tends to cause popping and loss of material upon subsequent ignition.

Alloy Steels: Nickel, Chromium-Nickel, Chromium-Vanadium, and Similar Low Alloy Steels Containing no Tungsten and Less than 5% of Chromium.—Proceed as with carbon steels.

High-Chromium Steels (Stainless, 18% chromium, 8% nickel, etc.).—Proceed with the perchloric acid method as directed for carbon steels after dissolving in a solution of equal parts of HCl and HNO_3.

Cast Iron.—Proceed as with carbon steel, using 2.336 g. of the sample for white irons and 0.9344 g. for gray irons.

Alloy Cast Irons.—For high chromium-nickel cast irons proceed as with carbon steels but dissolve the sample in a mixture of 20 ml. of HCl and 20 ml. of HNO_3.

COPPER BY THE ELECTROLYTIC OR GRAVIMETRIC METHOD

Special Solutions Required. *Diluted Sulfuric Acid (1 : 9).*—Slowly stir 100 ml. of H_2SO_4 into 900 ml. of water.

Acidulated H_2S Water.—Saturate 500 ml. of diluted H_2SO_4 (1 : 99) with H_2S.

Sodium Hydroxide (5%).—Dissolve 50 g. of NaOH in 1000 ml. of water.

Procedure. *Copper Steels: (a) Preliminary Separation.*—Transfer 5 g. of the sample to a 600-ml. beaker, add 200 ml. of diluted H_2SO_4 (1 : 9), and heat gently until action ceases. Dilute to 350 ml. with water, heat to boiling, and

[31] For high-silicon alloys, dissolve the sample in 40 ml. of diluted HCl (1 : 1), carefully oxidize with HNO_3, and then add the $HClO_4$. See p. 1422 for precautions when using $HClO_4$.

saturate with H_2S as the solution is allowed to cool during the course of 25 min. Allow the precipitate to settle, filter on paper or paper pulp, and wash a few times with diluted H_2SO_4 (1 : 99) that has been saturated with H_2S.

Transfer the residue and paper to a 25- or 35-ml. tall-form porcelain crucible, ignite at a temperature not exceeding 550° C., and fuse with 2 to 4 g. of alkaline pyrosulfate. Dissolve the cooled melt in 25 ml. of diluted HCl (1 : 9), dilute the solution to 100 ml.,[32] neutralize with a solution of NaOH (5%), and add approximately 0.3 ml. in excess. Boil for 3 min., digest for about 30 min., filter, and wash five or six times with a cool solution of NaOH (0.5%).

Dissolve the precipitate in 15 to 25 ml. of hot diluted HNO_3 (1 : 3), wash the paper with hot water, add 5 ml. of H_2SO_4 and evaporate until fumes of H_2SO_4 appear. Cool the solution, dilute to 40 ml., add an excess of several milliliters of NH_4OH, and heat to boiling. Allow the precipitate to settle, filter into a 250-ml. beaker, and wash with hot water. If more than 4 mg. of iron, tin, chromium, or other elements precipitable by NH_4OH, appear to be present, dissolve the precipitate in 15 to 25 ml. of hot diluted HNO_3 (1 : 3), and repeat the precipitation with NH_4OH. Filter and combine the filtrates. The further treatment depends on whether the copper is to be determined by electrolysis, or by precipitating as the sulfide and igniting to the oxide. The former method is to be preferred in analyses of the highest accuracy, and if over 0.25% of copper is present.

(*b*) ***Determination of Copper by Electrolysis: Apparatus.***—Direct current must be provided. The most satisfactory electrodes are platinum cylinders made from 50- to 60-mesh, sand-blasted gauze, stiffened by doubling the gauze for about 3 mm. at the top and bottom and supported by a platinum stem which is flattened and welded the entire width of the gauze.

Procedure.—Transfer the ammoniacal solution to a 250-ml. beaker, neutralize with diluted H_2SO_4 (1 : 1), and add an excess of 5 ml. of diluted H_2SO_4 (1 : 1) and also 4 ml. of diluted HNO_3 (1 : 1). Dilute the solution to 200 ml. Adjust the anode and weighed cathode, cover the beaker with split watch glasses, and electrolyze with a current of 0.5 amp. until the solution becomes colorless (about 2 hrs.). Rinse the cover glasses and the exposed stems of the electrodes and sides of the beaker. Continue the electrolysis for 30 min. and test for complete deposition (0.3 to 0.5 ml. of the electrolyte should not give a brown color with 0.3 to 0.5 ml. of freshly prepared H_2S-water). When deposition is complete, lower the beaker while washing the cathode with a stream of water. When free from electrolyte, detach the cathode, dip it in alcohol, shake off the excess, and dry for 1 min. at 100° C. Cool in a desiccator and weigh. The increase in weight multiplied by 20 represents the percentage of copper in the material.[33]

(*c*) ***Determination of Copper by Weighing as Oxide. (Copper less than 0.25%).***—Neutralize the ammoniacal solution obtained in (*a*) with diluted H_2SO_4 (1 : 1), add 4 ml. of the diluted acid in excess, and adjust the volume to about 100 ml. Heat to boiling and saturate with H_2S as the solution cools.

[32] If an appreciable amount of silica has separated, it may be removed by filtration before proceeding further.

[33] Deposits of copper may be removed by immersing the cathode in diluted HNO_3 (1 : 1), rinsing with water, then boiling with fresh HNO_3 for 5 to 10 min., rinsing with water and then strongly igniting for 10 to 25 min. over one or two large Méker burners.

Allow to settle, filter, transfer all the precipitate to the paper, and wash thoroughly with diluted H_2SO_4 (1 : 99) that has been saturated with H_2S. Transfer the paper and precipitate to a small porcelain or quartz crucible that has been weighed with cover. Heat under good oxidizing conditions until carbon has been destroyed, and then ignite to constant weight at 900° to 1000° C. Cover, cool over a good desiccant, and weigh as CuO. If a 5-g. sample was used, the weight of CuO multiplied by 16 represents the percentage of copper in the material.

Carbon Steels.—Use a 10-g. sample and proceed as with copper steels.

Alloy Steels.—Most alloy steels may be analyzed as described for carbon steels.

Tungsten Steels.—Treat 5-g. of the sample with 100 ml. of diluted HCl (1 : 1). Carefully add 20 ml. of diluted HNO_3 (1 : 1), and boil gently until the tungstic acid becomes bright yellow. Dilute the solution to 150 ml. with boiling water, digest for a few minutes, filter and wash with diluted HCl (1 : 9). Any copper retained in the tungstic acid is recovered as follows: Treat the residue with NH_4OH, add 5 g. of tartaric acid and sufficient H_2SO_4 to have an excess of 5 ml. per 100 ml. of solution. Treat with H_2S, filter and combine with the main sulfide precipitate.

Add 15 ml. of H_2SO_4 to the filtrate, evaporate just to fumes of H_2SO_4, cool, and add 100 ml. of water. If a small residue of tungstic acid separates, filter and wash with diluted H_2SO_4 (5 : 95). Add 5 g. of tartaric acid to the clear filtrate, neutralize with NH_4OH, adjust the acidity to 5% by volume with H_2SO_4, heat to boiling, and pass a rapid stream of H_2S into the solution for 10 to 15 min. Let the precipitate settle, filter, wash, and complete the determination as directed for carbon steels.

Cast Iron.—Dissolve 5 g. of the sample in 100 ml. of diluted H_2SO_4 (1 : 5). When solution is complete evaporate to fumes of H_2SO_4, cool somewhat, dilute to 100 ml. with warm water, heat until salts have dissolved, and filter. Wash the residue with hot water, dilute the filtrate to 500 ml. with hot water, and proceed as with carbon steel. In very accurate work the residue shall be examined for copper.

Wrought Iron and Open-Hearth Iron.—Proceed as with copper steels, using 10-g. of the sample.

COPPER BY THE THIOSULFATE–IODIDE METHOD

Special Solutions Required. ***Sodium Thiosulfate (50%).***—Dissolve 100 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 100 ml. of water and filter if a residue remains.

Standard Sodium Thiosulfate.—Dissolve 5 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 500 ml. of recently distilled water, add 0.1 g. of Na_2CO_3 and dilute to 1 liter. To standardize, transfer 0.05 g. of pure metallic copper to a 150-ml. beaker, cover and dissolve the metal in 4 to 5 ml. of diluted HNO_3 (sp.gr. 1.20). Boil gently to expel oxides of nitrogen. Cool, add NH_4OH until the solution just turns blue, add acetic acid, etc., and complete the titration as described in the method.

Starch Solution.—See the determination of Sulfur by the Evolution Method.

Procedure. ***Copper Steels.***—Transfer 5 g. of the sample to a 600-ml. beaker, add 100 ml. of diluted H_2SO_4 (1 : 9), and heat gently until action ceases. Dilute to 250 ml., heat to boiling, add 10 ml. of the solution of $Na_2S_2O_3 \cdot 5H_2O$

(50%) and continue the boiling for 5 to 10 min. or until the precipitate settles rapidly. Filter immediately, transfer all the precipitate to the paper, and wash the paper and precipitate well with diluted H_2SO_4 (1 : 99) that has been saturated with H_2S. Place the paper and precipitate in a porcelain or silica crucible, dry and ignite at a *low* temperature (520° to 550° C.; conveniently in a muffle furnace) until all carbon is destroyed. Cool, transfer the contents of the crucible to a 250-ml. beaker. Add 5 to 6 ml. of diluted HNO_3 (sp.gr. 1.20) [34] to the crucible, warm gently and pour upon the residue in the beaker. Rinse the crucible with a little water and warm the beaker and contents until the copper oxide has dissolved. Carefully evaporate the solution to a volume of 2 to 3 ml. in order to expel most of the acid.[34] Cool, add 90 ml. of water,[35] and add either 10 ml. of a solution of ammonium bifluoride (20%), or 1 g. of sodium fluoride (to prevent interference by ferric iron). Then add NH_4OH until the solution just reacts alkaline to litmus. Cool the solution to room temperature. Acidify with acetic acid (80%) and add 1 ml. of the acid in excess. Add 3 to 4 g. of KI which has been dissolved in a little water, stir well, and immediately titrate with the standard thiosulfate. When the brown tints have nearly disappeared, add 5 ml. of starch solution and continue the titration until one drop changes the color from blue to yellowish white, and remains permanent for 15 to 20 sec.

Carbon Steel.—Use 10 g. of the sample and proceed as with copper steel.

Alloy Steels.—Most alloy steels may be analyzed as described for copper or carbon steels.

Tungsten Steels.—Treat 5 g. of the sample with 75 ml. of diluted HCl (1 : 1). Carefully add 15 ml. of diluted HNO_3 (1 : 1) and boil gently until the tungstic acid becomes bright yellow. Dilute the solution to 100 ml. with boiling water, digest for several minutes, filter, and wash with diluted HCl (1 : 9). For recovery of copper held by tungstic acid, see the determination of copper in tungsten steels by the electrolytic method.[36]

Add 10 ml. of H_2SO_4 to the filtrate and evaporate to fumes of sulfuric acid. Cool, dilute to 200 ml., heat to boiling, add 60 ml. of the thiosulfate solution, boil for 5 min., and complete the determination as described for copper steels.

Cast Iron.—Dissolve 5 g. of the sample in 100 ml. of diluted H_2SO_4 (1 : 4). When solution is complete, evaporate to copious fumes of sulfuric acid. Cool somewhat, dilute to 100 ml. with warm water, heat until salts have dissolved, filter, and wash the residue with hot water. Dilute the filtrate to 250 ml., heat to boiling, add 20 ml. of thiosulfate solution, continue the boiling for 5 min. and complete the determination as described for copper steels.

Wrought Iron and Open-Hearth Iron.—Use 10 g. of the sample and proceed as described for copper steels.

[34] Alternately, the residue on the paper may be dissolved in hot diluted HNO_3 (1 : 2) and the solution caught in the original beaker, and 5 ml. of diluted sulfuric acid (1 : 1) added. Then evaporate the solution to copious fumes, cool, dilute to 50 ml., treat with HF, NH_4OH, etc., and complete the titration with thiosulfate as directed.

[35] Since molybdenum interferes partly in this method, it is necessary, if the steel contains more than 0.25% of molybdenum, to separate the latter from copper by treatment at this point with NaOH as directed in the electrolytic or gravimetric method.

[36] See p. 1448.

NICKEL BY THE DIMETHYLGLYOXIME METHOD

Special Solutions Required. ***Dimethylglyoxime Solution*** ***(1%)***.—Dissolve 10 g. of dimethylglyoxime in 1000 ml. of ethyl or methyl alcohol, or diluted NH_4OH (13 : 7). Ten milliliters of this solution allows sufficient excess to precipitate completely 0.015 g. of nickel. The alcoholic solution keeps almost indefinitely; the ammoniacal solution does not keep as well, and no more of it should be prepared than can be used in a week. Occasionally NH_4OH contains impurities which cause incomplete precipitation of nickel.

Tartaric Acid Solution ***(25%)***.—Dissolve 250 g. of tartaric acid in 600 ml. of water, filter, add 10 ml. of HNO_3, and dilute to 1 liter.

Procedure. ***Nickel Steels*** ***(0.05 to 3.5% nickel)***.—Transfer 1 g. of the sample [37] to a 400-ml. beaker, cover, and treat with 60 ml. of diluted HCl (1 : 1).[38] Warm until decomposition is complete, and then cautiously add 10 ml. of diluted HNO_3 (1 : 1). Boil until iron and carbides are oxidized and oxides of nitrogen have been expelled. Dilute to 200 ml. with hot water. Add 20 ml. of a solution of tartaric acid (25%), neutralize with NH_4OH and add 1 ml. in excess. Filter if any insoluble matter (such as silica) is present, and wash the paper and residue with hot water containing a little NH_4OH and NH_4Cl. Add HCl until slightly acid, warm to about 60° to 80° C. and add 20 ml. of an alcoholic or ammoniacal solution of dimethylglyoxime (1%). Add NH_4OH until slightly alkaline, and digest for 30 min. at about 60° C.[39]

(*a*) ***Gravimetric Method.***—Filter through a weighed Gooch crucible under light suction, but do not allow the mat to run dry. Wash the precipitate thoroughly with hot water. Add 5 ml. of dimethylglyoxime reagent to the filtrate and washings, stir, and allow to stand to determine whether precipitation is complete. Dry the precipitate for 1 hr. at 110° to 120° C., and weigh as the salt $NiC_8H_{14}O_4N_4$ which contains 20.32% of nickel. Porous crucibles or crucibles containing glass frit may also be used. If glass frit crucibles are used, it is advisable to allow a thin mat of the precipitate to form before strong suction is applied. The precipitate may also be caught on filter paper and ignited at about 800° C. to the oxide, NiO. In this case, care shall be taken to prevent sublimation of the glyoxime before it is decomposed. This is done by enclosing the wet paper and precipitate in one or two wet ashless papers and igniting so that the papers char before taking fire.

If appreciable cobalt (over 1%) or copper (over 4%) is present, add sufficient glyoxime to take care of them as well as the nickel, and preferably reprecipitate the nickel as follows: When the precipitate has been washed, discontinue the suction, place the original beaker under the funnel, and add 25 ml. of a hot mixture of 20 ml. of diluted HCl (1 : 1) and 5 ml. of HNO_3. After 1 min. apply suction until dry, repeat the treatment with 25 ml. of acid mixture,

[37] If the steel contains less than 1% of nickel, 2- or 3-g. samples may be used with correspondingly larger amounts of tartaric acid. For steels containing more than 3.5% of nickel, either a sample equivalent to about 0.035 g. of nickel, or a suitable aliquot portion of a larger sample may be used.

[38] If the percentage of chromium is less than 0.5%, the sample may be dissolved in 50 ml. of hot diluted HNO_3 (1 : 3).

[39] If the amount of nickel is small (under 0.2%), or if much cobalt is present, the solution should be allowed to stand at room temperature overnight and filtered cold. In routine analyses involving more than 2 mg. of nickel and no appreciable amounts of cobalt, the solution may be filtered within 5 min. after adding the glyoxime and stirring.

drain, and wash thoroughly with 50 ml. of hot water containing 1 g. of tartaric acid. Nearly neutralize the absolutely clear solution with NH_4OH and precipitate with dimethylglyoxime and NH_4OH as before. A glyoxime precipitate contaminated by cobalt is a darker red than a pure nickel dimethylglyoxime.

(*b*) ***Electrolytic Method.***—Occasionally in umpire analyses, and with high-nickel steels the determination is best completed by the electrolytic method as follows: Filter the nickel dimethylglyoxime precipitate on a 12 or 15-cm. paper and wash thoroughly 18 to 20 times with hot water. Dissolve the precipitate in hot diluted HNO_3 (1 : 3) and wash the filter thoroughly with hot water. Add 20 ml. of diluted H_2SO_4 (1 : 1) and evaporate to strong fumes of sulfuric acid. Cool somewhat, add 10 ml. of HNO_3, and repeat the evaporation to fumes. Rinse the cover and sides of the beaker with water and fume the solution again to insure the expulsion of every trace of the HNO_3. Cool, add 50 ml. of cold water, and heat until salts are dissolved.

Neutralize with NH_4OH and add an excess of 25 ml. of NH_4OH. Dilute to 175 ml. and electrolyze with a current of from 1 to 2 amp. using a weighed platinum gauze cathode and a spiral platinum anode. Continue the electrolysis until the solution has become colorless (5 to 8 hrs.). The solution may be tested for complete electrolysis by adding one or two drops of it to 1 ml. of a solution of potassium thiocarbonate.[40] A pink or red color indicates the presence of nickel. Without interrupting the current, wash the cathode with cold water as it is withdrawn from the solution. Dip the cathode into a beaker of water and then into alcohol, dry for a few minutes at 100° C., cool, and weigh.

The increase in weight of the cathode multiplied by 100 and divided by the weight of the sample taken gives the percentage of nickel in the sample. In very accurate work, dissolve the deposit in warm HNO_3, wash the cathode with water, then alcohol, dry for a few minutes at 80° C., and reweigh.

High-Chromium High-Nickel Steels (***20% chromium, 20% nickel***; ***18% chromium, 8% nickel, etc.***).—Transfer 0.35 to 0.5 g. of the sample to a 400-ml. beaker, and treat with 20 ml. of diluted HCl (1 : 1) and 20 ml. of diluted HNO_3 (1 : 1). Heat until solution ensues, add 15 ml. of diluted H_2SO_4 (1 : 1), and evaporate just to light fumes (for low-carbon, low-silicon alloys this latter step may be omitted). Cool somewhat, and add 100 ml. of water. Warm until salts dissolve, filter, and proceed as directed for nickel steels, sufficient dimethylglyoxime being added to precipitate all of the nickel (20 to 40 ml. of a 1% solution).

Carbon Steels, and Other Steels with less than 0.05% Nickel.—Transfer 5 g. of the sample to a 400-ml. beaker, add 40 ml. of diluted HCl (1 : 1). Heat until solution ensues and then carefully add 15 ml. of diluted HNO_3 (1 : 1). Evaporate to a volume of about 15 ml. and add 50 ml. of diluted HCl (sp.gr. 1.12). Transfer to a 200-ml. separatory funnel, rinsing the beaker with several 15-ml. portions of the diluted HCl (sp.gr. 1.12). Cool to 10° C., add 120 ml. of ether, and carefully shake for 1 to 2 min. in a stream of cold water. Let settle for several minutes and then draw off the lower clear solution into the original beaker. Gently heat the solution in the beaker to expel the ether (avoid free flames), add 0.3 g. of $KClO_3$, boil until the chlorate is decomposed,

[40] Prepared by saturating one-half of a solution of KOH (5%) with H_2S, adding the other half, and heating *moderately* with one twenty-fifth of its volume of CS_2. The dark red liquid is decanted from the undissolved CS_2 and kept in a well-closed flask.

dilute to 100 ml., and add 3 g. of tartaric acid. Make the solution alkaline with NH_4OH and filter. Acidify with HCl and complete the determination as directed for nickel steels.

Cast Irons.—Dissolve 5 g. of the iron in 40 ml. of diluted HCl (1 : 1), carefully add about 15 ml. of diluted HNO_3 (1 : 1) to oxidize the iron, and evaporate to dryness. Drench the hot dried mass with 10 ml. of HCl and then dilute with 75 ml. of hot water. Filter, wash with diluted HCl (sp.gr. 1.12) and evaporate the filtrate to a syrupy consistency. Add 50 ml. of diluted HCl (1 : 1), transfer to a 200-ml. separatory funnel, rinse the beaker with several small portions of the diluted HCl (1 : 1), add 120 ml. of ether, and complete the determination as directed for carbon steels.

High-Nickel Chromium Alloy Cast Irons (15% nickel, 6% copper, 2% chromium, etc.).—Transfer a 2.5-g. sample to a 400-ml. beaker or flask and treat with a mixture of 25 ml. of HCl and 25 ml. of HNO_3. When solution is complete add 30 ml. of $HClO_4$, 5 to 10 drops of HF, and fume for 10 to 15 min. after the chromium has been oxidized. Cool somewhat, add 100 ml. of water and heat to boiling. Filter and wash well with diluted HCl (5 : 95), catching the filtrate and washings in a 250-ml. volumetric flask.[41] Mix the contents, cool to room temperature, adjust to the mark and mix thoroughly. Pipette out 50-ml. aliquot portions and proceed by the glyoxime-electrolytic method as directed for nickel steels. Either dissolve and reprecipitate the nickel glyoxime, or determine any occluded copper in the deposit and correct for same.

Open-Hearth Iron.—Proceed as with carbon steels.

Wrought Iron.—Proceed as with carbon steels.

Nickel Wrought Iron.—Proceed as with nickel steels, but dissolve the first glyoxime precipitate and again precipitate nickel with dimethylglyoxime as directed in the procedure with cobalt steels.

NICKEL BY THE CYANIDE TITRATION METHOD

Special Solutions Required. *Sulfuric-Citric Acids.*—Dissolve 200 g. of citric acid in a cooled mixture of 100 ml. of H_2SO_4 and 900 ml. of water.

Standard Silver Nitrate Solution.—Dissolve 5.789 g. of $AgNO_3$ in water and dilute to exactly 1000 ml. Each 1 ml. of this solution is equivalent to 0.001 g. of nickel.

Standard Potassium Cyanide Solution.—Dissolve 4.5 g. of KCN in 1000 ml. of water containing 1 g. of KOH. Standardize against a steel of known nickel content by applying the method described in the procedure below. The cyanide changes with age so its titer should be checked frequently.

Procedure. (*a*) *Direct Titration.*—This method is not applicable to steels containing copper, cobalt or more than 1% of tungsten. Copper reacts like nickel, and divalent cobalt not only consumes cyanide but also causes trouble in obtaining an end point. A fairly satisfactory end point, representing both nickel and cobalt, can be obtained by first oxidizing the cobalt in ammoniacal-citrate solution to the trivalent state with $NaClO_3$.

[41] The residue sometimes contains appreciable amounts of nickel. This may be recovered by igniting, treating with HF, evaporating and fusing the residue with a small amount of $K_2S_2O_7$, dissolving and adding to the main solution.

Nickel Steels.—Transfer 1 g. of the sample to a 400-ml. beaker, treat with 20 ml. of diluted HNO_3 (1 : 1) and heat until solution is complete.[42] Add 10 ml. of a solution of $(NH_4)_2S_2O_8$ (15%), and boil for 5 min. Cool, and add 50 ml. of the sulfuric-citric acid solution. Immediately add NH_4OH until the solution assumes a greenish tint, dilute to 200 ml. and complete the neutralization as follows: Add exactly 2 ml. of the standard $AgNO_3$, and, if no precipitate appears, add diluted HCl (1 : 10) until a precipitate of AgCl forms. Then add diluted NH_4OH (1 : 1), dropwise, with constant stirring until the precipitate just dissolves. Add 3 ml. of NH_4OH (sp.gr. 0.90), 2 ml. of a solution of KI (10%), and titrate with standard KCN with continuous stirring until the solution becomes perfectly clear. Determine the volume of KCN equivalent to exactly 2 ml. of the standard $AgNO_3$. Subtract this quantity from the volume of KCN and multiply by the nickel titer of the cyanide solution.

(*b*) ***Following a Preliminary Precipitation by Dimethylglyoxime.***—This method may be applied to steels containing cobalt, copper and tungsten. The silver and cyanide solutions are the same as described in (*a*) but instead of standardizing these solutions against a standard steel the theoretical titer of $AgNO_3$ is taken as standard and the equivalent of the KCN is found by titration in a water solution containing no iron or citrate.

Nickel Steels.—Precipitate the nickel in a 1-g. sample as described for nickel steels by the dimethylglyoxime method.[43] Dissolve the washed precipitate with a hot mixture of 20 ml. of diluted HCl (1 : 1) and 5 ml. of HNO_3 in a 400-ml. beaker.[44] Evaporate the solution to 50 ml. or until free from dimethylglyoxime and oxidizing gases. Cool the solution, dilute to 150 ml., add exactly 2 ml. of the standard $AgNO_3$, neutralize with NH_4OH, and complete the titration as described in (*a*).

(*c*) ***Following a Preliminary Extraction with Ether.***—This method is not applicable to steels containing cobalt, or more than 1% of tungsten.

Nickel Steels.—Transfer 1 g. of the sample to a 150-ml. beaker, cover, and treat with 20 ml. of diluted HCl (sp.gr. 1.12). When reaction ceases, carefully add 4 ml. of diluted HNO_3 (1 : 1), and boil to expel oxides of nitrogen. Cool, transfer the solution to a 200-ml. separatory funnel, and rinse the beaker with diluted HCl (sp.gr. 1.12). Cool to 10° C., add 40 ml. of ether (perform this operation away from open flames or hot plates), shake gently for a few minutes, let settle for 2 min., and draw off the acid layer into a 250-ml. beaker. Add 5 ml. of diluted HCl (sp.gr. 1.12) to the ether portion. Cool, shake, let settle for 1 min., draw off the acid layer and add it to the main extract. Heat gently to expel dissolved ether, add 0.2 g. of $KClO_3$, and boil until the chlorine is driven off. Dilute to 100 ml. with water, neutralize with NH_4OH, add an excess of 3 to 4 ml. and boil for a few minutes. Filter and wash with hot water. To the filtrate, add 10 ml. of HCl, heat just short of boiling, and treat with H_2S. Filter and wash with acidulated H_2S water. Boil to expel H_2S, dilute to 200 ml., neutralize with NH_4OH, and proceed with the titration as described in (*a*).

[42] If the steel contains more than 1% of chromium, decompose the sample in 20 ml. of diluted H_2SO_4 (1 : 4), oxidize by carefully adding 5 ml. of HNO_3, boil for 5 min., cool, and add the sulfuric-citric acid mixture.

[43] See p. 1450.

[44] If the steel contains more than 4% of copper, or 2% of cobalt, the nickel should be reprecipitated with glyoxime. See dimethylglyoxime method.

Carbon Steels.—Transfer 5 g. of the sample to a 400-ml. beaker, add 40 ml. of diluted HCl (1 : 1). Heat until solution ensues, then carefully add 15 ml. of diluted HNO_3 (1 : 1). Evaporate to a volume of about 15 ml., add 50 ml. of diluted HCl (1 : 1), and extract with 120 ml. of ether as directed for carbon steels by the dimethylglyoxime method.[45] Heat the acid extract gently to expel dissolved ether, add 0.3 g. of $KClO_3$ and complete the determination as described in (*c*).

Cast Irons.—Dissolve 5 g. of the iron in 40 ml. of diluted HCl (1 : 1), carefully oxidize with HNO_3, and evaporate to dryness. Dilute, filter and extract with ether as directed for carbon steels by the dimethylglyoxime method.[45] Complete the determination as described in (*c*).

CHROMIUM BY THE PERSULFATE OXIDATION METHOD

Special Solutions Required. ***Sulfuric-Phosphoric Acid Mixture.***—Mix 320 ml. of diluted H_2SO_4 (1 : 1), 80 ml. of H_3PO_4 (85%) and 600 ml. of water.

Silver Nitrate (1%).—Dissolve 10 g. of $AgNO_3$ in 1000 ml. of water.

Ammonium Persulfate (15%).—Make up as needed by dissolving 15 g. of the salt in 100 ml. of water.

Standard Potassium Permanganate Solution (0.06 N, approximately).—Dissolve 2 g. of $KMnO_4$ in 1000 ml. of water. Let age for 1 week or more. Filter through purified asbestos and standardize against the National Bureau of Standards' standard sample 40*c* of sodium oxalate as follows: Transfer 0.2 g. of the standard sodium oxalate to a 400-ml. beaker. Add 150 ml. of diluted H_2SO_4 (5 : 95), previously boiled for 10 to 15 min. and then cooled to 27° C. ±3° C. Stir until the oxalate has dissolved. Add 40 to 42 ml. of the $KMnO_4$ (0.06 N) at a rate of 25 to 35 ml. per min., while stirring slowly. Let stand until the pink color disappears. (If the pink color should persist because the permanganate is too strong, discard, and begin again, adding a few less milliliters of the $KMnO_4$ solution.) Heat to 55° to 60° C. and complete the titration by adding permanganate until a faint pink color persists for 30 sec. Add the last 0.5 to 1 ml. dropwise, with particular care to allow each drop to become decolorized before the next is introduced. Determine the excess of permanganate required to impart a pink color to the solution by matching the color in another beaker containing the same amount of the specially treated diluted H_2SO_4 at 55° to 60° C. One milliliter of exactly 1 N $KMnO_4$ is equivalent to 0.01734 g. of chromium.

Standard Ferrous Sulfate.—Dissolve 32 g. of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in a cool mixture of 50 ml. of H_2SO_4 and 950 ml. of water. To obtain the ratio of the $FeSO_4$ solution to the $KMnO_4$ solution, take 25 ml. of the former, dilute to 350 ml. with cool diluted H_2SO_4 (5 : 95), add 2 ml. of H_3PO_4 and titrate with $KMnO_4$ solution to a faint permanent pink tint. Determine the blank on the same volume of water and acids, deduct, and calculate the volume of $KMnO_4$ solution which is equivalent to 1 ml. of the $FeSO_4$ solution. The ratio of the $FeSO_4$ solution to $KMnO_4$ must be determined daily unless the ferrous solution is kept under hydrogen. Stronger solutions of $FeSO_4$ and $KMnO_4$ may, of course, be prepared for use with high-chromium steels. Ap-

[45] See p. 1451.

proximately 0.1 N solutions are desirable with material containing over 3% of chromium.

Procedure. *Chromium Steels.*—With steels containing less than 2% of chromium, transfer 2 g. of the sample to a 600-ml. beaker and add 60 ml. of acid mixture. Heat until action ceases, cautiously add 10 ml. of diluted HNO_3 (1 : 1), and boil until all carbides are dissolved and oxides of nitrogen are expelled. With steels containing between 2 and 5% of chromium, dissolve 1 g. of the sample, evaporate until salts separate, dilute with about 50 ml. of warm water, add 5 to 10 ml. of HNO_3, and again carefully evaporate until salts separate. If carbides still persist, filter, wash the paper with warm water, ignite the paper and residue, fuse with sodium carbonate, and add the solution of the melt to the main solution. After the sample is completely dissolved dilute to 300 ml. with hot water and add 5 ml. of the $AgNO_3$ (1%) and 20 ml. of the $(NH_4)_2S_2O_8$ (15%). Boil the solution for 8 to 10 min. If the color of $KMnO_4$ does not develop add more $AgNO_3$ and $(NH_4)_2S_2O_8$ and again boil for 10 min. Add 5 ml. of diluted HCl (1 : 3) and continue the boiling for 5 min. after the pink color has just disappeared. If the $KMnO_4$ is not destroyed by boiling for 10 min., or if a precipitate of MnO_2 remains, add 2 to 3 ml. more of diluted HCl (1 : 3) and boil as before. The total period of boiling after the addition of $(NH_4)_2S_2O_8$ shall not be less than 15 min.; 30 min. will do no harm.[46] Cool the solution, dilute to 400 ml., and add a measured volume of the standard $FeSO_4$ solution (25 ml. for less than 1.5% chromium steel, 50 ml. for 1.5 to 3% chromium, etc.). Stir and titrate with the standard $KMnO_4$[47] until an end point is obtained which is permanent upon continued stirring for 1 min.[48] The titration must be corrected for dilution effect and color interference. The correction may be made (1) empirically; [49] (2) by titrating the same volume

[46] Chromium (and vanadium) may also be oxidized to Cr_6 (and V_5) with hot concentrated $HClO_4$. See p. 1422 for precautions when using $HClO_4$. Unless special precautions are taken, oxidation of chromium does not quite reach 100%. The oxidation procedure is as follows: Transfer the sample (depending on the chromium content, 0.5 g. for stainless and 2 g. for 1 to 3% chromium steels) to a 500-ml. tall-form beaker (Pyrex) or 500-ml. Soxhlet flask (Pyrex) and cover with a watch glass. If a flask is used the watch glass should be raised by a small glass hook to avoid subsequent formation of a liquid seal. A stirring rod placed inside the vessels will also prevent bumping tendencies. Add 20 to 25 ml. (depending on the weight of the sample) of perchloric acid (60%). A technical grade of acid is satisfactory and cheaper. Warm until the steel is dissolved and boil gently for 20 min. Cool *rapidly*, by immersing the vessel in cold water for one-fourth of a second, withdraw rapidly, and then immerse a second time and swirl for 8 to 10 sec. Add an equal volume of water and boil 3 min. to remove chlorine. Cool, dilute to 200 to 250 ml., and titrate with $FeSO_4$–$KMnO_4$ as directed.

[47] In the absence of tungsten, the end point may be obtained by potentiometric titration with standard $FeSO_4$ solution. In this case, the ferrous solution is standardized with recrystallized $K_2Cr_2O_7$. Vanadium is included in this titration. If present, it must be determined and subtracted from the apparent chromium value (vanadium, per cent $\times 0.339$ = chromium, per cent). With tungsten steels the potentiometric procedure is modified by omitting H_3PO_4 and oxidizing tungsten to tungstic acid with HNO_3 (when H_3PO_4 is added to hold tungsten in solution the potentiometric end point with $FeSO_4$ is difficult to detect).

[48] In the absence of vanadium the first end point is permanent, but if vanadium is present, the end point will fade at first, owing to the slow oxidation of vanadium from the quadrivalent to the quinquevalent stage in a cold solution.

[49] In this correction the dilution effect is ignored and the volume of $KMnO_4$ used in overcoming the green color is taken as equivalent to 0.6% of the chromium present. The correction is usually applied to the titer of the solution, as, for example, by using the titer 0.01744 g. of chromium instead of 0.01734 g. per milliliter of 1 *N* solution.

of $FeSO_4$ solution in a solution of like volume and acidity and containing the same amounts of the coloring elements in their final valencies; or (3) by a second titration of the final solution. The last is the most convenient and satisfactory in occasional analyses, and may be performed by boiling the solution which has just been titrated for 10 min. in order to destroy the slight excess of permanganate, cooling to room temperature, and then titrating with $KMnO_4$ to the color that was originally taken as the end point. The solution can be used for the determination of vanadium.[50]

$$\text{Chromium in 2-g. sample, per cent} = (A \times B) - (C - D) \times 50\ E$$

where A = the volume of $FeSO_4$ solution,
B = the volume of $KMnO_4$ solution which is equivalent to 1 ml. of $FeSO_4$ solution,
C = the volume of $KMnO_4$ solution,
D = the correction for the end point, and
E = the chromium titer of the $KMnO_4$ solution.

If the solutions are equivalent and a 2-g. sample is used, calculate the chromium as follows:

$$\text{Chromium in 2-g. sample, per cent} = A - (C - D) \times 50\ E$$

High-Chromium High-Nickel Steels.—Transfer 0.5 g. to a 600-ml. beaker and treat with 75 ml. of diluted H_2SO_4 (1 : 4). When solution is complete evaporate to salts, cool, dilute to 70 ml., and dissolve the iron salts. Oxidize the iron by the cautious addition of HNO_3. Add 3 to 4 drops of HF and again evaporate just to salts. Cool, dilute to 300 ml. with hot water, add 10 ml. of the $AgNO_3$ solution, 15 g. of $(NH_4)_2S_2O_8$, and boil the solution for 10 to 12 min. Add 5 ml. of diluted HCl (1 : 3) and complete the determination as in chromium steels. Stronger solutions of $FeSO_4$ and $KMnO_4$ are more convenient for use with high-chromium steels.

The visual end point in high-chromium steels can be detected more easily when oxidation-reduction indicators are used, that is, ortho-phenanthroline ferrous complex for the $FeSO_4$-$K_2Cr_2O_7$. With *o*-phenanthroline (1 to 2 drops of the 0.025 Molar indicator) the end point in the $FeSO_4$-$KMnO_4$ titration is indicated by the change in color from pink to clear green (permanent for 60 sec.). With diphenylaminesulfonic acid, the chromic acid is titrated with the $FeSO_4$ solution to a clear green end point. The $FeSO_4$ solution in this case is standardized either on a standard chromium steel or pure $K_2Cr_2O_7$. Vanadium, if present, will also be titrated as in the potentiometric method. When *o*-phenanthroline is used the vanadium may be determined in the same solution, after the initial end point is obtained, by reducing the acidity of the solution with sodium acetate and titrating slowly at 50° C. with the standard $KMnO_4$ (0.05 N) to the green end point.

Carbon Steels and Other Steels with less than 0.15% Chromium.—Transfer 10 g. of the sample [51] to a 500-ml. Erlenmeyer flask, add 110 ml. of diluted

[50] See the Determination of Vanadium in Chromium-Vanadium Steels by the Ferrous Sulfate-Potassium Permanganate Method, p. 1459.

[51] Larger or smaller samples may be taken, but the volume of acid shall be varied accordingly. A good rule to follow is to use the equivalent of 1 ml. of concentrated H_2SO_4 for each 1 g. of steel and then 1 ml. in excess.

H_2SO_4 (exactly 10% by volume). Heat to boiling, boil until reaction is complete and then dilute with 100 ml. of boiling water. Add a solution of $NaHCO_3$ (8%) from a burette until a permanent precipitate appears (approximately 36 ml. with carbon steels) and then 4 ml. in excess. Boil for 1 min., let settle, filter on a rapid filter, and quickly wash the flask and precipitate two or three times with hot water. If the precipitation has been properly performed, there will be no more precipitate than can be conveniently handled on an 11-cm. paper. The filtrate will become cloudy in the funnel stem and in the receiving vessel on account of oxidation and hydrolysis. Ignite the residue in a nickel or iron crucible (free from chromium) and fuse with ten or twelve times its volume of Na_2O_2 (free from chromium). Dissolve the cooled melt by immersing it in 100 ml. of cold water, remove the crucible, add 1 g. of Na_2O_2 and boil for 5 to 10 min. or allow to stand on the steam bath for 30 min. Filter through an asbestos pad,[52] preferably on a small Büchner funnel, and wash with a cold solution of NaOH (2%) containing 1% of Na_2SO_4. Dilute to a measured volume and compare the color with a standard solution of $K_2Cr_2O_7$ containing approximately the same concentration of chromium and alkali.

To prepare the standard solution, dissolve 0.283 g. of $K_2Cr_2O_7$ in water and dilute to exactly 1000 ml. Each 1 ml. shall correspond to 0.1 mg. of chromium. When these solutions are used, they shall be made alkaline to compare with the solution under test. Solutions containing from 2 to 10% of NaOH and 1 mg. of chromium per 100 ml. are suitable for the colorimetric comparisons.

If the color of the unknown solution is too deep for convenient colorimetric comparison, the solution may be boiled *thoroughly* to decompose all the peroxide, acidified, and one of the titration procedures applied.

***Cast Iron** (less than 0.15% chromium).*—Proceed as with carbon steels.

***Cast Iron** (over 0.15% chromium).*—Transfer 2 g. of the sample to a 600-ml. beaker and add 60 ml. of the sulfuric-phosphoric acid mixture. Heat until action ceases, add 15 ml. of diluted HNO_3 (1 : 1) and boil until the oxides of nitrogen are expelled. Evaporate until salts separate, dilute with about 50 ml. of warm water and digest until salts are dissolved. Filter and wash the paper with warm water. If chromium is less than 0.75%, the residue will be practically free from chromium. To recover any insoluble chromium, ignite the paper and insoluble matter until all carbon is consumed. Treat the residue with HF and H_2SO_4, fuse with Na_2CO_3, and add the solution of the melt to the main solution. To the latter add 5 ml. of the $AgNO_3$, dilute to 300 ml. with boiling water and complete the determination as directed for chromium steels.

***High-Nickel Chromium Alloy Cast Irons** (15% nickel, 6% copper, 2% chromium, etc.).*—Transfer 2 g. of the sample to a 500-ml. Erlenmeyer flask and add 20 ml. of a mixture of equal parts of HCl and HNO_3. Heat until action ceases. Then add 15 ml. of $HClO_4$ (60%), 5 drops of HF and evaporate to fumes on a hot plate. Fume 1 to 2 min. over an open flame and then 10 min. more on a hot plate. Cool somewhat, add 50 ml. of water and transfer to a 600-ml. beaker. Add 20 ml. of H_2SO_4, dilute to 300 ml. and complete the determination by the persulfate-silver nitrate method.

Open-Hearth Iron.—Proceed as with carbon steels.

Wrought Iron.—Proceed as with carbon steels.

[52] Asbestos is more satisfactory than filter paper. If paper is used, it shall first be thoroughly washed with a solution of NaOH (5%) in order to remove soluble organic matter.

VANADIUM BY THE ELECTROLYTIC SEPARATION METHOD

Special Solutions Required. ***Diluted Sulfuric Acid*** ***(1 : 9)***.—Slowly stir 100 ml. of H_2SO_4 into 600 ml. of cool water, cool, and then dilute to 1000 ml. It is important that this acid be of the indicated strength.

Sodium Bicarbonate ***(8%)***.—Dissolve 80 g. of $NaHCO_3$ in 1000 ml. of water.

Potassium Ferricyanide.—Prepare a very dilute solution as needed, by dissolving a crystal the size of the head of a pin in 25 ml. of water.

Standard Potassium Permanganate.—Prepare as described under the determination of chromium in chromium steels by the persulfate oxidation method.

Procedure. ***Vanadium Steels.***—Transfer 2 g. of the sample to a 300-ml. Erlenmeyer flask, and add 30 ml. of diluted H_2SO_4 (exactly 10% by volume). When action is complete, dilute to 100 ml. with boiling water and heat to boiling. Agitate gently while adding $NaHCO_3$ solution from a burette until a permanent precipitate is formed, and then add 4 ml. more. Cover the flask, boil for 1 min., and let the precipitate settle. Filter rapidly, conveniently by moderate suction through a cone and paper containing some paper pulp, and wash the flask and precipitate four or five times with hot water. The filtrate will become cloudy in the funnel stem and receiving vessel because of oxidation and hydrolysis of the iron, but this is of no consequence. Place the paper and precipitate in the original flask, add 20 ml. of HNO_3, shake until the paper has broken up, and add 5 ml. of H_2SO_4. Heat over a free flame until fumes of H_2SO_4 are given off. Cool, and, if organic matter is still present, add more HNO_3 and repeat the treatment. Finally cool, wash down the flask, and evaporate until it is certain that HNO_3 has been completely expelled. Cool, dilute to 40 ml.,[53] neutralize the solution with NH_4OH, add H_2SO_4 till acid and then add an excess of 0.5 ml. per 100 ml. of solution. Transfer the solution to the electrolyzing apparatus, rinsing the flask with small portions of water. The electrolysis may be performed with a mercury cathode in (1) a special modified funnel.[54] (2) in an ordinary beaker with a sealed-in platinum wire, or (3) in an ordinary beaker with the cathode wire enclosed in a glass tube extending into the mercury. In any case, the cathode wire shall be embedded in

[53] If tungsten is present, the solution must be filtered, the tungstic acid washed with diluted H_2SO_4 (1 : 99) its vanadium content determined colorimetrically and added to that found by titration. The colorimetric test shall be made as follows. Dissolve the tungstic acid in a solution of NaOH, or fuse the ignited impure oxide with Na_2CO_3 and extract the melt with water. Filter if not clear, and dilute to 75 to 100 ml. Add H_3PO_4 (sp.gr. 1.37) until acid, then a 5-ml. excess, and let stand for 1 to 2 hrs. Compare the yellow solution of vanadotungstic acid with a standard prepared by adding from a burette a standard solution of vanadotungstic acid to water until the intensity of color in the solution is the same when the solutions are of equal volume. The standard solution of vanadotungstic acid shall be prepared as follows: Dissolve 2.5 g. of sodium tungstate and enough sodium vanadate to give exactly 0.05 g. of vanadium in 100 ml. of water. Dilute to 200 ml., add 25 ml. of H_3PO_4 (sp.gr. 1.37), and dilute to exactly 500 ml. Ammonium salts cannot be used as they give rise to turbid solutions. If only ammonium vanadate is available, dissolve it in water, expel all ammonia by boiling with a slight excess of NaOH, and acidify with H_3PO_4.

The vanadium held by the tungsten approximates 0.01 mg. of vanadium per 0.01 g. of tungsten and, in routine analyses, the correction is made by calculation, that is, 0.018% vanadium is added for an 18% tungsten steel.

[54] Melaven cell, see A. S. Melaven, "Electrolytic Cell for Use with the Mercury Cathode," Industrial and Engineering Chemistry, Analytical Edition 2, p. 180 (1930).

about 200 g. of mercury, and the solution electrolyzed using a current density of approximately 0.16 amp. per sq. cm. as the solution is stirred or agitated. Continue the electrolysis until iron is absent as indicated by a ferricyanide test on a small drop of the electrolyte. This should not require more than 45 min. When *all* the iron has been removed, draw off the electrolyte, and wash the mercury two or three times with water while the current is continued.[55] In these operations care shall be taken to prevent any amalgam from passing into the electrolyte.[56] Add 2 to 3 ml. of diluted H_2SO_4 (1 : 1), heat to 70° to 80° C., and add $KMnO_4$ solution until a strong pink color appears. Heat to boiling, and pass a current of SO_2 into the solution until the vanadium is reduced (2 to 5 min.).[57] Continue the boiling, and pass a rapid stream of CO_2 (free from O_2) until the solution is free from SO_2. This may be ascertained by passing the gas issuing from the flask into 5 ml. of water containing a drop of diluted H_2SO_4 (1 : 1) and enough $KMnO_4$ to give a faint pink tint. Cool the solution to 60° to 80° C., and titrate with the $KMnO_4$ (0.03 N). Repeat the reduction and titration until concordant results are obtained. Correct the titration by a blank determination (usually amounting to about 0.1 ml.) of the $KMnO_4$ (0.03 N) on a solution of like volume and acidity. To obtain the percentage of vanadium, multiply the corrected volume by the vanadium titer of the solution, multiply by 100, and divide by the weight of the sample.

Carbon Steels.—Proceed as with vanadium steels but treat 5 g. of the sample with 60 ml. of diluted H_2SO_4 (exactly 10% by volume).

Cast Iron.—Proceed as with carbon steels.

Open-Hearth Iron.—Proceed as with carbon steels.

Wrought Iron.—Proceed as with carbon steels.

VANADIUM BY REDUCTION WITH FERROUS SULFATE AND TITRATION WITH PERMANGANATE [58]

Special Solutions Required.—See the special solutions required in the determination of Chromium by the Persulfate Oxidation Method.

Procedure. ***Chromium-Vanadium Steels.***—After the determination of chromium, by the persulfate oxidation method, add 5 ml. of H_3PO_4 (85%), unless the solution already contains it, and then add 15 ml. of a solution of

[55] To clean the mercury, transfer it to a large flask, add diluted HNO_3 (1 : 9) containing a little $NaNO_2$ and agitate the mercury by drawing air through it for several hours. Remove the acid, add a fresh portion of acid, and agitate again. Draw off the second portion of acid, add water and repeat the agitation. Repeat the treatment with water to remove all acid.

[56] With chromium steels it is usually necessary, because of the brittle chromium amalgam, to filter the electrolyte through a rapid filter and wash with water.

[57] The direct use of a solution of H_2SO_3 or an alkali sulfite is unwise unless it has been freshly prepared, for after a lapse of time they contain oxidizable bodies other than sulfurous acid or sulfite. Sulfur dioxide is most conveniently used from a cylinder of the liquefied gas, or it may be obtained as wanted by heating a flask containing a solution of H_2SO_3 or a sulfite to which diluted H_2SO_4 (1 : 1) is added.

[58] Where apparatus for potentiometric titrations is available, oxidation with HNO_3 is a very satisfactory method for the determination of vanadium, particularly for chromium-tungsten-vanadium steel. The sample is treated with 100 ml. of diluted H_2SO_4 (1 : 4) and then with HNO_3 to oxidize iron (and tungsten). After dilution to 200 ml. and addition of 40 ml. of HNO_3 (sp.gr. 1.42), the solution is boiled for 35 to 45 min., cooled, and titrated potentiometrically with $FeSO_4$.

$FeSO_4$ (0.03 N approximately) (1 ml. will reduce 0.0015 g. of vanadium) if vanadium is under 0.8%, and proportionately more if the percentage exceeds this amount. If enough has been added, a drop of the solution will give immediately a blue color with a drop of fresh $K_3Fe(CN)_6$ solution. Stir the solution thoroughly, add 8 ml. of a freshly prepared solution of $(NH_4)_2S_2O_8$ (15%), and stir for 1 min. Titrate with the $KMnO_4$ (0.03 N) to a definite pink tint which does not fade upon continued stirring for 1 min. Subtract the same blank as was determined in the determination of chromium in chromium steels.[59]

If a correction for the end point has not been determined in a prior determination of chromium, or if the chromium value is unknown and an empirical correction is therefore impossible, the blank shall be obtained at this point as follows: Boil the solution for 10 to 12 min. to destroy the slight excess of $KMnO_4$, cool to room temperature and titrate with the $KMnO_4$ solution to the same tint as was obtained before. The volume required represents the blank.[60] The vanadium may then again be reduced by an excess of $FeSO_4$ and the solution treated with $(NH_4)_2S_2O_8$, etc., as a check on the first. The percentage of vanadium is calculated by multiplying the corrected volume of $FeSO_4$ solution by the vanadium titer of the solution, dividing by the weight of sample, and multiplying by 100.

Chromium-Tungsten-Vanadium Steels.—Transfer 2 g. of the sample to a 600-ml. beaker, and add 100 ml. of diluted H_2SO_4 (1 : 9). Heat until action ceases, add 10 ml. of diluted HNO_3 (1 : 1) and 4 ml. of diluted HCl (1 : 1) and boil the solution gently for about 30 min. or until the tungsten has been oxidized to yellow tungstic acid. Stir frequently to break up the film adhering to the sides and bottom of the beaker. Dilute to 100 ml., filter through a light filter paper and wash with diluted H_2SO_4 (1 : 200).[61] Dilute the filtrate to 300 ml., add 5 ml. of H_3PO_4 and then $KMnO_4$ until the solution is pink. From this point proceed with the addition of $FeSO_4$ as described for chromium-vanadium steel.

Carbon Steels (less than 0.05% vanadium).—Transfer a 10-g. sample to a 500-ml. Erlenmeyer flask, make a bicarbonate separation, fuse, and dissolve the melt as described for the determination of chromium in carbon steels by the persulfate oxidation method.[62] Acidify with H_2SO_4 and H_3PO_4 and complete the titration as with chromium-vanadium steel. As an alternate procedure, 10 g. of the sample may be treated with cupferron as described in the following section for chromium-nickel steels.

High-Chromium High-Nickel Steels.—Treat 10 g. of the sample (less than 0.05% vanadium) in a 400-ml. beaker with 250 ml. of diluted H_2SO_4 (8 : 92) and

[59] According to the Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels, p. 47 (1921), the correction amounts to 0.02% +1.8% of the percentage of chromium present. For example, if Cr = 1.5%, the blank due to chromium is 0.018×1.5 or 0.03%, and the total correction is 0.02 + 0.03 or 0.05% of vanadium.

[60] The blank may also be obtained by means of a standard steel of known vanadium content and containing about the same amount of chromium as the test sample.

[61] The vanadium content of the tungstic acid may be determined by igniting, fusing with Na_2CO_3, extracting with water and proceeding as described in the colorimetric test given under the determination of Vanadium in Vanadium Steels by the Electrolytic Separation Method, p. 1458.

[62] See p. 1456.

heat gently until action ceases. (For vanadium steels, use a 2-g. sample and 150 ml. of diluted H_2SO_4 (5 : 95).) Cool the solution to 15° C. and add a goodly amount of paper pulp. Then add dropwise with constant stirring a cold, freshly prepared 6% solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5N \cdot NO \cdot ONH_4$) until the precipitate just assumes a reddish brown color. Filter through an 11-cm. paper containing some paper pulp, and wash 10 to 12 times with cold diluted sulfuric acid (1 : 99). Transfer the paper and contents to the original beaker, add 20 ml. of HNO_3 and 10 ml. of H_2SO_4. Evaporate to fumes of H_2SO_4. Cool, add 10 ml. of HNO_3 and again evaporate to copious fumes of H_2SO_4. Cool, dilute to 300 ml. add 3 ml. of H_3PO_4 (85%) and then $KMnO_4$ until the solution is pink. From this point proceed with the addition of $FeSO_4$ as described for chromium-vanadium steel.

Cast Iron (*less than 0.05% vanadium*).—Proceed as with carbon steels.

Open-Hearth Iron.—Proceed as with carbon steels.

Wrought Iron.—Proceed as with carbon steels.

MOLYBDENUM BY THE α-BENZOINOXIME METHOD [63]

Special Solutions Required. *α-Benzoinoxime* (*2%*).—Dissolve 10 g. of α-benzoinoxime in 500 ml. of ethyl alcohol. Filter if not clear.

Boric Acid (*4%*).—Dissolve 4 g. of boric acid in 100 ml. of water.

Procedure. *Molybdenum Steels.*—Transfer 1 to 3 g. of the sample to a 600-ml. beaker, add 50 ml. of diluted H_2SO_4 (1 : 6) and warm until action ceases. Carefully add just enough HNO_3 to decompose carbides and to oxidize iron and molybdenum. Add 2 to 4 drops of HF, mix and then add 10 ml. of the boric acid solution.[64] Boil for a few minutes and filter if the solution is not perfectly clear.[65]

Dilute to 100 ml. with water, cool to 25° C., and add sufficient $FeSO_4$ (0.5 g. is usually sufficient) to reduce vanadic and chromic acids. Cool to 5° C., stir, and slowly add 10 ml. of the α-benzoinoxime solution and 5 ml. extra for each 0.01 g. of molybdenum present. Continue to stir the solution, add just enough bromine water to tint the solution a pale yellow, and then add a few more milliliters of the benzoin reagent. Allow the beaker and contents to remain in the cooling mixture 10 min. with occasional stirring, stir in a little macerated filter pulp, and filter through a rapid paper. If the first 50 ml. or so are not entirely clear, this portion shall again be filtered. Wash the precipitate with 200 ml. of a cold, freshly prepared solution containing 25 to 50 ml. of the prepared reagent and 10 ml. of H_2SO_4 in 1000 ml. On standing, needlelike crystals will appear in the filtrate if sufficient reagent has been employed.

Transfer the precipitate and paper to a platinum crucible and cautiously dry. Char, without flaming, and ignite at 500° to 525° C. Cool, weigh, and

[63] H. B. Knowles, "The Use of α-Benzoinoxime in the Determination of Molybdenum," Bureau of Standards Journal of Research, 9, No. 1, July, 1932, Research Paper 453.

[64] With larger samples (5 to 6 g.) of silicon steel it is best to evaporate the solution, dehydrate, and remove silica before treatment with the benzoin reagent.

[65] Alternately, the sample may be dissolved in a mixture of HCl and HNO_3, $HClO_4$ added and the solution evaporated to fumes of $HClO_4$, diluted, sufficient H_2SO_3 added to reduce the chromium, and, after boiling out the excess SO_2 and filtering off any silica, cooled and molybdenum then precipitated.

repeat the heating until the weight remains constant. Treat the ignited residue with 5 ml. of NH_4OH, digest, and filter through a small paper. Wash well with diluted NH_4OH (1 : 99). Ignite the paper and contents in the original crucible, cool, and weigh. The difference in weights represents the MoO_3 present.

Tungsten is also precipitated. If present, the ammoniacal filtrate shall be treated as follows: Add 5 ml. of diluted H_2SO_4 (1 : 1) and evaporate to fumes of H_2SO_4. Cool, dilute to 25 ml. with water, add 1 to 2 ml. of cinchonine solution (125 g. of cinchonine dissolved in 1000 ml. of diluted HCl (1 : 1)). Digest at 80° to 90° C., preferably overnight. Filter through a tight paper containing a little paper pulp and wash with cinchonine wash solution (30 ml. of the cinchonine solution diluted to 1000 ml.). Transfer the paper and contents to a platinum crucible, char the paper and ignite at 750° to 850° C. until constant weight is obtained. Cool, weigh, and subtract from the weight of MoO_3 obtained previously. In very accurate work any residue obtained here shall be dissolved and tested for molybdenum by the colorimetric method.[66]

With high-molybdenum medium-tungsten steel (8% molybdenum, 2% tungsten) the ignited oxides may be weighed, dissolved, and molybdenum determined by the MoS_3-MoO_3 (after reprecipitation of the sulfide) method. Tungsten is then obtained by difference.

If molybdenum is present in very small amounts (carbon steels), the ignited α-benzoinoxime precipitate shall be dissolved in NH_4OH and the molybdenum determined colorimetrically.[66]

Cast Iron.—Transfer 1- to 5-g. of the sample to a 600-ml. beaker, treat with 100 ml. of diluted H_2SO_4 (1 : 4) and warm. When action ceases, add HNO_3 dropwise until rapid effervescence ceases (usually 2 to 5 ml.) and then add 2 to 3 drops in excess. Evaporate the solution to fumes of H_2SO_4, cool somewhat, and add 100 ml. of water. Warm until salts are dissolved and filter through a rapid paper. Wash the paper with warm water. Dilute the filtrate to 150 ml. and cool to 25° C. Add sufficient $FeSO_4$ to reduce any chromium or vanadium which may have been oxidized by the above treatment, cool to 5° C. and complete the determination as directed for molybdenum steels.

Open-Hearth Iron.—Proceed as with molybdenum steels.

Wrought Iron.—Proceed as with molybdenum steels.

MOLYBDENUM BY PRECIPITATION AS SULFIDE AND WEIGHING AS OXIDE

Procedure. ***Molybdenum Steels*** **(*Absence of Tungsten*).**—Transfer 2 to 10 g. of the sample (approximately 0.03 g. molybdenum) to a 600-ml. beaker, treat with 100 ml. of diluted H_2SO_4 (1 : 5), and warm. When action ceases, add 20 ml. of a solution of $(NH_4)_2S_2O_8$ (25%) and boil the solution for 8 to 10 min. to oxidize the molybdenum and part of the iron. Cool somewhat, add 5 g. of tartaric acid, neutralize with NH_4OH, add diluted H_2SO_4 (1 : 1) until acidified and then 10 ml. in excess for each 100 ml. of solution. Heat to boiling and pass in a rapid stream of H_2S for 10 min. Dilute with an equal volume of hot water, and pass in the gas for 5 min. Digest at 50° to 60° C. for 1 hr.

[66] See p. 1464.

Filter and wash the sulfur and sulfides with diluted H_2SO_4 (1 : 99) saturated with H_2S.[67] Place the paper and precipitate in the original beaker,[68] add 5 ml. of H_2SO_4 and 20 ml. of HNO_3, cover, and heat to fumes of H_2SO_4. Cool somewhat, add 10 ml. of HNO_3 and again evaporate to fumes. If the solution is not clear and of a light color, repeat the treatment with HNO_3.

Cool, dilute to 100 ml., and add a slight excess (10 to 12 drops) of a solution of NaOH (20%). Heat to boiling and set aside for 5 min. Filter and wash the paper and residue with hot water. Heat the filtrate to boiling and treat with H_2S for 10 min. Add diluted H_2SO_4 (1 : 1) until acidified and then a 4 ml. excess per 100 ml. of solution. Treat with H_2S for 5 min. and digest at 50° to 60° C. for 1 hr. Filter through a tight 9-cm. filter paper, and wash thoroughly with diluted H_2SO_4 (1 : 99) saturated with H_2S.[69] Transfer to a small porcelain crucible, heat carefully until carbon is destroyed and then at 500° to 525° C. until constant weight is obtained.[70] Test the ignited oxide for impurities by treating with NH_4OH. If copper is indicated, determine its amount colorimetrically, calculate to CuO and deduct. If a residue remains, filter, wash with water, ignite, weigh, and deduct from the weight of MoO_3.[71] The factor for molybdenum in MoO_3 is 0.667.

Tungsten Steels.—Dissolve 2 to 10 g. of the sample (approximately 0.03 g. of molybdenum) in 100 ml. of diluted HCl (1 : 1), cautiously add 20 ml. of diluted HNO_3 (1 : 1), and then boil gently until the tungstic acid becomes bright yellow. Dilute to 150 ml., heat to boiling, filter, and wash the residue with diluted HCl (1 : 9). Reserve the precipitate. Add 15 ml. of H_2SO_4 to the filtrate, evaporate to fumes of H_2SO_4, cool, and add 100 ml. of water. Digest until soluble salts are in solution. If any tungstic acid separates, filter through a small filter, wash with a little diluted H_2SO_4 (1 : 99), and combine with the reserved tungstic acid precipitate. Add 5 g. of tartaric acid to the clear filtrate

[67] In umpire analyses the filtrate shall be boiled to expel H_2S and its molybdenum content determined colorimetrically, or the unprecipitated molybdenum (usually not in excess of 0.5 mg.) shall be recovered as follows: Boil the filtrate to expel H_2S and to reduce the volume to about 450 ml. Add 20 ml. of the persulfate solution, boil for 8 to 10 min., and then pass in a rapid stream of H_2S for 10 to 15 min. Digest for 1 hr., filter, wash, and combine with the main precipitate.

[68] An alternate method for routine analyses consists in directly igniting the impure sulfide at 500° to 525° C., weighing and then correcting the weight of the ignited residue as follows: To the crucible add diluted HCl (1 : 1) and heat until the residue is dissolved. Transfer the solution to a small beaker, dilute to about 100 ml., and add NaOH in slight excess (10 drops of a 20% solution). Boil for 1 min., allow the precipitate to settle, and filter. Dissolve the precipitate in diluted HCl (1 : 1), and precipitate with NaOH as before. Wash the paper and precipitate thoroughly with water to remove alkali salt; ignite the paper and precipitate in the original crucible, and weigh. The difference between the two weights represents MoO_3.

[69] Precipitation of molybdenum is usually complete, but it is well to test the filtrate by boiling to expel H_2S, oxidizing with bromine water, boiling to expel bromine, and again gassing with H_2S.

[70] Molybdenum oxide volatilizes at temperatures above 500° C. but the rate is very slow at temperatures below 600° C. The heating may be done in a muffle with pyrometer, or in a "radiator." This is a 50-ml. porcelain crucible containing a disk of asbestos board, 4 mm. thick on the bottom and fitted with a nichrome triangle which is bent to fit the inside of the crucible and supported by bending the end wires over the rim. The crucible shall be placed so that the bottom is 8 cm. above the top of a Tirrill burner and heated by a flame 12.5 cm. high.

[71] If small amounts of molybdenum are in question, the determination shall be checked by testing the solution of the oxide as described in the colorimetric method.

and neutralize with NH_4OH. Add H_2SO_4 until acidified, then 5 ml. per 100 ml. in excess, and pass in H_2S as in the absence of tungsten.

Some molybdenum is always carried down by the tungstic acid and shall be recovered as follows: Dissolve the combined tungstic acid residues in a hot solution of NaOH (5%), and wash the papers with a little water and then with a little hot diluted H_2SO_4. Add 5 g. of tartaric acid, then H_2SO_4 until the solution contains 5 ml. per 100 ml., and precipitate with H_2S as in the absence of tungsten. Filter, wash, combine with the main sulfide precipitate, and complete the determination as described for molybdenum steels.

Cast Iron.—Transfer 2- to 5-g. of the sample to a 600-ml. beaker, treat with 100 ml. of diluted H_2SO_4 (1 : 4), and warm. When action ceases, add diluted HNO_3 (1 : 1) dropwise until rapid effervescence ceases (usually 5 to 10 ml.) and then add three to five drops in excess. Evaporate the solution to fumes of H_2SO_4. Cool somewhat, add 100 ml. of warm water, stir, and heat until salts are dissolved. Filter through a rapid filter paper catching the filtrate in a 600-ml. beaker. Wash the paper well with hot water. To the filtrate add 5 g. of tartaric acid and neutralize the solution with NH_4OH. Add 10 ml. of diluted H_2SO_4 (1 : 1) for each 100 ml. of solution, heat to boiling, and pass in a rapid stream of H_2S for 10 min. Dilute with an equal volume of hot water, and pass in the gas for 5 min. Digest at 50° to 60° C. for 1 hr., filter, and complete the determination as described for molybdenum steels.

Carbon Steels.—Proceed as with molybdenum steels.

Open-Hearth Iron.—Proceed as with molybdenum steels.

Wrought Iron.—Proceed as with molybdenum steels.

MOLYBDENUM BY THE COLORIMETRIC METHOD

Special Solutions Required. ***Sodium Thiocyanate*** *(5%).*—Dissolve 50 g. of the salt in 1000 ml. of water.

Stannous Chloride.—Transfer 350 g. of $SnCl_2 \cdot 2H_2O$ to a 500-ml. Erlenmeyer flask, add 200 ml. of diluted HCl (1 : 1), and boil gently until solution is practically complete. Transfer the solution to a 1-liter bottle, dilute to 1000 ml. with freshly boiled water, add a few pieces of metallic tin, and stopper.

Butyl Acetate.—Saturate technical butyl acetate with NaCNS and $SnCl_2$ by shaking, and keep in a dark bottle.

Standard Molybdenum Solution.—Dissolve 0.5 g. of pure $Na_2MoO_4 \cdot 2H_2O$ in 1000 ml. of water containing 5 ml. of H_2SO_4, and standardize by reducing 100 ml. of the solution in a Jones reductor and titrating with $KMnO_4$. Each 1 ml. of the solution should contain approximately 0.0002 g. of molybdenum. The standard solution may also be made from National Bureau of Standards' standard sample 71 of calcium molybdate.

Procedure.—Transfer 0.5 g. of the sample (for steels and irons containing 0.25% or less of molybdenum) to a 150-ml. Erlenmeyer flask. (For alloys containing 0.25 to 0.50% of molybdenum use 0.2 g. of the sample, and if over 0.5% 0.1 g. of the sample.) Add 20 ml. of $HClO_4$ (60%) per 1 g. of sample and warm until the sample has dissolved. Heat to boiling, cover, and fume until all carbonaceous matter has been destroyed. Cool somewhat, add 25 ml. of water, and boil for a few minutes to expel free chlorine.

Add 2 g. of tartaric acid and a slight excess of a solution of NaOH (10%). Heat at about 80° C. for a few minutes. Remove from the source of heat, neutralize with diluted H_2SO_4 (1 : 1) and then for each 8 ml. of solution add an excess of 2 ml. of the H_2SO_4 (1 : 1), which will give a solution of 10% H_2SO_4 by volume. Cool to room temperature and transfer the solution to a 250-ml. separatory funnel, rinsing out the flask with H_2SO_4 (10%). Add 10 ml. of a solution of NaCNS (5%). Shake vigorously for 30 sec., treat with 5 ml. of the $SnCl_2$ solution and shake well for 1 min. Cool to room temperature, add 20 ml. of treated butyl acetate, or 50 ml. of treated ethyl ether,[72] stopper, and shake well. Allow the extract to separate and draw off the lower layer which may be discarded. Transfer the extract [73] into a Nessler, Julian, or colorimeter tube (for example, Kennicott) and compare with a standard similarly carried through all steps of the procedure.[74] The standard steel may be prepared by adding portions of a standard molybdenum solution to a molybdenum-free steel, or a standard molybdenum steel may be used.

TUNGSTEN BY THE ACID DIGESTION-CINCHONINE METHOD

Special Solutions Required. *Cinchonine.*—Dissolve 125 g. of cinchonine in 1000 ml. of diluted HCl (1 : 1).

Cinchonine Wash Solution.—Dilute 30 ml. of the above solution to 1000 ml.

Procedure. *Tungsten Steels.*—Transfer 2 g. (for steels containing less than 5% of tungsten use 5 g.) of the sample to a 400-ml. beaker,[75] cover, and treat with 50 ml. of HCl. Warm gently. When decomposition is complete, cease heating, and scrub with a policeman to detach carbides and tungsten. Gradually add 10 ml. of diluted HNO_3 (1 : 1).[76] Digest at 100° C. with occasional stirring until the tungstic acid is bright yellow and free from black particles. Dilute to 150 ml., add 5 ml. of cinchonine solution and a small amount of paper pulp. Digest at 90° to 95° C. for 30 min. or longer as the solution is stirred occasionally.[77] Decant the clear solution through an ashless paper containing a little ashless paper pulp. Wash by decantation with two or three 30- to 40-ml. portions of hot cinchonine washing solution, transfer the residue to the paper,[78] and wash the paper and residue thoroughly with the washing solution.

[72] For satisfactory color comparisons the concentration of molybdenum should not exceed 0.05 mg. per milliliter of solvent.

[73] On very low molybdenum material it is of advantage to add another portion of NaCNS and $SnCl_2$, mix in the separatory funnel and again extract.

[74] If the extract is turbid, it should be filtered through a layer of glass wool.

[75] Smooth (unetched) beakers should be used because tungstic acid has a tendency to stick rather tenaciously to the vessel.

[76] Less vanadium in vanadium steels is retained in the tungstic acid when iron and tungsten are oxidized with H_2O_2. If the latter is to be used add to the partially cooled solution 6 ml. of perhydrol (30%) diluted with 14 ml. of water and boil gently until the volume has been reduced to about 25 ml. Dilute to 200 ml., add cinchonine, etc.

[77] Small amounts of tungsten separate slowly in the presence of considerable iron. Consequently, with less than 2% of tungsten, let the solution stand for 18 to 24 hrs. It has been stated that a more rapid precipitation of tungsten by cinchonine results if the iron is reduced to the bivalent state. This may be obtained conveniently by treating with sulfur dioxide.

[78] Dissolve any WO_3 that still adheres to the beaker, by adding a few drops of NH_4OH. Evaporate just to dryness and then add 2 to 3 ml. of diluted HCl (1 : 9) and 0.5 ml. of cinchonine solution. Heat to boiling, digest a few minutes, and pour onto the filter.

Transfer to a weighed platinum crucible, and ignite at as low a temperature as possible until carbon is gone. Treat with 1 or 2 drops of diluted H_2SO_4 (1 : 1) and 1 to 3 ml. of HF. Evaporate to dryness, ignite at 750° to 850° C., cool, and weigh as "impure WO_3." Add 4 g. of Na_2CO_3, and heat gradually until fusion is complete. Cool, take up the melt in 100 ml. of water, and filter. Thoroughly wash the crucible and residue, and reserve the filtrate. Transfer the residue to the crucible, ignite, fuse with 1 g. of Na_2CO_3, cool and take up in 25 ml. of water. Filter and thoroughly wash the crucible, paper, and residue with hot water. Combine the filtrate with the reserved filtrate. Again transfer the residue to the crucible and ignite. Cool, weigh, correct for the residue obtained from 5 g. of Na_2CO_3,[79] and subtract the corrected weight from the weight of "impure WO_3."

If the combined filtrates show a yellow color, evaporate to 100 ml. and determine chromium colorimetrically (as under the determination of chromium in carbon steels). Calculate to Cr_2O_3, and deduct from the weight of "impure WO_3." Divide the solution into three equal parts. In one aliquot portion determine molybdenum oxide, MoO_3, by the colorimetric method. In the second aliquot portion determine vanadium pentoxide, V_2O_5, by the colorimetric method,[80] adding one-third as much chromate to the comparison solution as was found in the colorimetric test. In the third aliquot portion separate tin, tantalum, columbium,[81] and the like by acidifying, adding NH_4OH in moderate excess and boiling. Filter, wash thoroughly, ignite, and weigh. Add the weights of the oxides found in the three aliquot portions, multiply by 3, and subtract from the weight of the "impure WO_3."

The final corrected weight of WO_3 multiplied by the factor 0.793, divided by the weight of sample taken, and multiplied by 100, represents the percentage of tungsten in the steel.

Carbon Steels and Other Steels Containing less than 0.2% Tungsten.— Transfer 5 g. of the sample to a 600-ml. beaker, add 75 ml. of diluted H_2SO_4 (1 : 6) and warm until action ceases. Carefully add just enough diluted HNO_3 (1 : 1) to decompose carbides and to oxidize the iron. Add about 5 mg. of molybdenum (conveniently, 25 ml. of the sodium molybdate solution).[82] Dilute to 150 ml., cool to 5° C. and precipitate with α-benzoinoxime. Determine tungsten subsequently in the mixed oxides as directed by precipitation with cinchonine as described for tungsten steels.

COBALT BY THE ZINC OXIDE–α–NITROSO–β–NAPHTHOL METHOD

Special Solutions Required. ***Zinc Oxide Suspension.***—Add 50 g. of the finely powdered reagent to 300 ml. of water and shake thoroughly.

[79] The residue obtained from the c.p. grade of Na_2CO_3 usually exceeds 1 mg. In analyses of 2-g. samples of a high-speed tool steel (18.23% tungsten, 3.51% chromium, and 0.97% vanadium), the correction for the impurities in the Na_2CO_3 averaged 1 mg. and the impurities in the "impure WO_3" averaged 5.8 mg. (representing 0.23% of tungsten). The weights of Fe_2O_3, Cr_2O_3, and V_2O_5 that were obtained ranged from 1.4 to 4.4 mg., 0.4 to 0.5 mg., and 1.4 to 2.7 mg., respectively.

[80] See the Determination of Vanadium in Vanadium Steels by the Electrolytic Separation Method, p. 1458.

[81] If a search is to be made for tantalum and columbium, the residue insoluble in Na_2CO_3 should also be examined, because part of these may be contained in it.

[82] See the standard molybdenum solution described under the determination of Molybdenum by the Colorimetric Method, p. 1464.

α-Nitroso-β-Naphthol.—Dissolve 1 g. of the dry reagent in 15 ml. of glacial acetic acid and filter.

Procedure. *Cobalt Steel.*—Transfer 1 g. of the sample to a 400-ml. beaker, add 25 ml. of diluted HCl (1 : 1), heat, and when decomposition is complete, add 5 ml. of diluted HNO_3 (1 : 1) to oxidize the iron. If tungsten is present the digestion with HNO_3-HCl shall be continued until all of the tungsten has been converted to yellow tungstic acid. Evaporate until salts begin to separate (about 5 ml.). Add 100 ml. of hot water, and digest on the steam bath for about 5 min. Dilute the solution to about 200 ml., and add a freshly prepared suspension of zinc oxide in portions of about 5 ml. until the iron is precipitated and a slight excess of zinc oxide is present. Shake thoroughly after each addition of the precipitant and avoid a large excess. When sufficient zinc oxide has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is also indicated by a slightly white and milky supernatant liquid. Allow the precipitate to settle for a few minutes and filter the solution through a 12.5-cm. rapid filter paper.[83] Wash the beaker and the precipitate on the filter three times with cold water. Reserve the filtrate and washings. When the filter has drained, transfer the paper and precipitate to the beaker in which the precipitation was made, add 12 ml. of HCl, and stir the paper to a pulp. The iron should now be in solution; if it is not, add more HCl, avoiding a large excess. Dilute the solution to 200 ml., and repeat the precipitation with zinc oxide. Filter on a 15-cm. paper, and wash four or five times with cold water.

For routine work, a single precipitation will often suffice. In this case take a 2-g. sample, dilute the solution to exactly 500 ml. after the addition of zinc oxide, mix thoroughly, and filter through a dry filter into a 250-ml. measuring flask (equals 1-g. sample). With one precipitation by zinc oxide, the percentages obtained for cobalt in high-speed steels will be from 0.1 to 0.3 too low as the result of retention of cobalt by the bulky precipitate.

To the combined filtrates and washings, from the zinc oxide separation, add 10 ml. of HCl, and adjust the volume to about 400 ml. Heat the solution to boiling, add 8 ml. of α-nitroso-β-naphthol solution plus 3 ml. in addition for every 0.01 g. of cobalt present. Allow the solution to cool for 30 min. or more, and filter through a rapid filter paper. Transfer all of the precipitate to the filter and wash with hot diluted HCl (1 : 3) and then thoroughly with hot water.

Transfer the wet paper and precipitate to a weighed porcelain crucible, heat gently at first, preferably in a muffle furnace, and finally ignite to constant weight at 750° to 850° C. Heating above 900° C. has a tendency to convert Co_3O_4 to CoO. Cool, and weigh as Co_3O_4 which contains 73.4% of cobalt. In very accurate work in which more than 0.01 g. of cobalt is involved, the oxide shall be reduced in hydrogen, cooled in an atmosphere of hydrogen, and the cobalt weighed as metal.[84]

Nickel accompanies cobalt almost completely in the zinc oxide separation. Hence, in very accurate work, when nickel predominates, or much of it is

[83] A little finely divided zinc oxide may pass through the paper at first. This is unobjectionable, because zinc is not precipitated by α-nitroso-β-naphthol.

[84] With high molybdenum or copper steels (over 1%), the ignited Co_3O_4, or cobalt metal may contain small amounts (approximately 0.5 mg.) of these elements. Suitable corrections may be made after solution of the residue and colorimetric determinations of the contaminants.

present, the ignited cobalt oxide should be dissolved in HCl and cobalt again precipitated with α-nitroso-β-naphthol.[85]

A blank shall be taken through all steps of the determination. A 1-g. sample of National Bureau of Standards' standard sample 10*d* of bessemer steel, or sample 50*a* of chromium-tungsten-vanadium steel is satisfactory for this purpose. It is especially important that the same quantity of the α-nitroso-β-naphthol be used in the blank run as in the determination. A little macerated paper added to the blank after the α-nitroso-β-naphthol reagent facilitates filtration and washing.

Carbon Steels (and Other Steels Containing less than 0.10% Cobalt).—Dissolve 10 g. of the sample in HCl and cautiously oxidize with just enough HNO_3. Extract the iron with ether and wash the ether extract once with diluted HCl. Warm the ether-extracted acid solution to expel residual ether, and oxidize with $KClO_3$. Dilute to 200 ml., and precipitate twice with zinc oxide as directed for cobalt steels. In material containing very little cobalt, it is advantageous to combine the extract acid solution obtained in ether separations of a number of separate 10-g. samples.

Cast Iron.—Proceed as with carbon steels.

Open-Hearth Iron.—Proceed as with carbon steels.

Wrought Iron.—Proceed as with carbon steels.

TITANIUM BY THE CUPFERRON–COLORIMETRIC METHOD

Special Solutions Required. ***Cupferron (6%).***—Dissolve 2 g. of the salt in 35 ml. of cold water. This reagent shall be prepared as needed.

Standard Titanium Solution.—The standard titanium solution is usually made from potassium titanium fluoride, $K_2TiF_6 \cdot H_2O$, as follows: Recrystallize the c.p. salt twice from hot water in a platinum dish. Filter, dry at room temperature, and preserve in a glass-stoppered bottle. Transfer 2.70 g. to a platinum dish, add 100 ml. of H_2SO_4, and evaporate 3 times to strong fumes of the acid, each time washing down the inside of the dish with water. Cool, and pour the solution rapidly and with stirring into 900 ml. of water. If the solution is properly made, it should be perfectly clear. Cool to room temperature, and transfer to a glass-stoppered bottle. Standardize by taking 50-ml. portions, precipitating with NH_4OH in a boiling 250-ml. solution, filtering, igniting at about 1200° C., and weighing as TiO_2. Each 1 ml. of the solution should contain 0.5 mg. of titanium.

Procedure. ***Titanium Steels.***—Transfer 0.5 to 1 g. of the sample to a 400-ml. beaker, add 100 ml. of diluted HCl (1 : 4), cover, and heat gently until action ceases. Cool the solution to 15° to 20° C., and add dropwise a cold, freshly prepared, solution of cupferron (6%), with constant stirring, until the precipitate just assumes a reddish brown color. Additional cupferron only causes more iron to be precipitated. Add a goodly amount of ashless paper pulp and filter through an 11-cm. rapid filter paper. Wash 12 to 15 times with cold diluted HCl (1 : 9). Transfer the paper and residue to a 50-ml. platinum crucible, dry, and ignite at a temperature (less than 500° C.) just sufficient to

[85] Tests on a 0.5-g. sample of a steel containing 10% of cobalt and 6% of nickel showed but 0.1 mg. of nickel in the first precipitate.

destroy the carbon of the filter paper. Fuse the contents of the crucible with 1 g. of $K_2S_2O_7$ and dissolve the cooled melt in 25 ml. of diluted H_2SO_4 (10 : 90).

Transfer the solution to a Camp or a Nessler comparison tube, and dilute to a suitable volume containing 10 ml. of H_2SO_4 per 100 ml. Add H_3PO_4 dropwise until any iron color is destroyed. To a second tube, add reagents K_2SO_4, H_3PO_4, etc. in amounts that are present in the unknown, and dilute with diluted H_2SO_4 (5 : 95) to the same volume. Cool both to room temperature. Add 3 ml. of H_2O_2 (3%) to each and then a standard solution of $Ti(SO_4)_2$ to the blank run and a similar volume of diluted H_2SO_4 (5 : 95) to the unknown until the colors match when the solutions are well mixed. The unknown then contains the amount of titanium that was added to the blank run. If a colorimeter of the plunger type is used, a suitable standard solution of peroxidized titanium may be prepared and the colors matched by changing the depths of the columns that are viewed. The amounts of titanium in the two solutions are then inversely proportional to the heights of the columns.

If the steel contains an appreciable amount of copper, filter the original H_2SO_4 solution of the sample through a small filter paper containing some paper pulp. Wash well with hot diluted H_2SO_4 (1 : 9). Cool the filtrate to 15° to 20° C. and precipitate with cupferron as described in the first paragraph. Transfer the paper containing the acid insoluble material to a 250-ml. beaker, add 25 ml. of diluted HNO_3 (3 : 7) and heat until the copper has dissolved. Add 50 ml. of hot water and a slight excess of NH_4OH. Heat to boiling, filter, and wash the paper and precipitate with hot water. Burn off the paper at as low a temperature as possible and add the residue to the ignited cupferron precipitate. Fuse the combined residues with $K_2S_2O_7$, dissolve in diluted H_2SO_4 (1 : 9) and determine colorimetrically as previously described. If the steel contains vanadium (more especially when small amounts of titanium are sought), transfer the ignited cupferron precipitate to a 100-ml. platinum dish, add 5 ml. of HF (48%), 10 ml. of $HClO_4$ and evaporate to a volume of 5 ml. or less. Cool somewhat, dilute to 50 ml. and add an excess of 5 ml. of the NaOH (10%). Boil for several minutes, let settle, and filter on a tight 9-cm. filter paper. Wash the paper and precipitate with hot water, ignite, fuse with a small amount of $K_2S_2O_7$, and complete the determination for titanium as described above.

Carbon Steels, Open-Hearth Iron, and Wrought Iron (***less than 0.05% titanium***).—Treat 5 g. of the sample with 150 ml. of diluted HCl (1 : 4) and proceed as described for titanium steels.

Cast Iron (***total titanium***).—Treat 5 g. of the sample with 100 ml. of diluted HCl (1 : 2), cover, and warm. When *all* action has ceased, cool to 10° C., add 1 ml. of a solution of cupferron (6%), filter on a paper of close texture, and wash the insoluble matter with water. Transfer the paper and residue to a platinum crucible, dry, and ignite under good oxidizing conditions in an uncovered crucible until all carbon is gone. Treat with 1 to 2 ml. of HF and 1 ml. of diluted H_2SO_4 (1 : 5), and evaporate to dryness. Fuse the residue with 1 to 2 g. of Na_2CO_3. Dissolve the melt in about 50 ml. of water, digest for 15 min. at 90° to 95° C., filter, and wash with water. Ignite the residue in platinum, and fuse with 1 to 3 g. of $K_2S_2O_7$. Cool, treat the melt with 25 ml. of diluted H_2SO_4 (1 : 9), transfer to a Camp or Nessler comparison tube, and determine the titanium colorimetrically as described for titanium steels.

Zirconium by the Cupferron—Phosphate Method

Procedure. ***Zirconium Steels.***—Transfer 2 to 3 g. of the sample to a 250-ml. beaker, add 100 ml. of diluted HCl (1 : 4), cover, and heat until action ceases. Dilute to 150 ml., cool to 15° to 20° C., precipitate with cupferron, filter, and fuse the ignited precipitate with $K_2S_2O_7$ as directed for titanium in titanium steels. Dissolve the cooled melt in 100 ml. of diluted H_2SO_4 (1 : 9), and filter through a small paper to separate any siliceous matter that may be present. Wash with diluted H_2SO_4 (1 : 9). To the filtrate add 2 ml. of H_2O_2 (30%) and a solution of 3 g. of $(NH_4)_2HPO_4$ in 25 ml. of water. Stir vigorously and let stand for 1 to 2 hr. at a temperature of 60 to 65° C. An excess of peroxide must be present at all times, and with amounts of zirconium under 0.01% the solution should be allowed to stand at room temperature overnight. Filter through a 9-cm. filter paper containing ashless pulp, and wash thoroughly with a cold solution of NH_4NO_3 (5%). Transfer the paper and residue to a platinum crucible, and ignite very carefully so that the paper chars but does not flame. When the paper has charred, gradually increase the temperature until all carbon is gone, and then heat at about 1050° C. for 15 min. Cool in a desiccator and weigh as ZrP_2O_7.

In very accurate analysis, the pyrophosphate shall be tested for titanium by fusing with 4 to 5 g. of $K_2S_2O_7$, and dissolving the melt in 40 ml. of diluted H_2SO_4 (1 : 9) containing 5 ml. of H_2O_2 (3%). If titanium is present, it is determined colorimetrically, calculated to $Ti_2P_2O_9$, and deducted from the weight of ZrP_2O_7.

Carbon Steels, Open-Hearth Iron, Wrought Iron and Cast Iron.—Treat 5 g. of the sample with 150 ml. of HCl (1 : 4) and proceed as for zirconium steels.

OTHER METHODS [86]

VOLUMETRIC DETERMINATION OF MAGNANESE—AFTER PERIODATE OXIDATION [87]

Chloride must be absent. Cobalt interferes as in the bismuthate method. When periodate is added to a solution of cobaltous sulfate, the solution becomes dark brown, owing to oxidation of the cobaltous salt. In steel containing 1.13% of manganese and 0.5% of cobalt, 1.32% of manganese was obtained. Cerium also interferes because it is oxidized to a ceric salt.

Procedure for Steel or Iron, Free from Chromium.—Dissolve 1 gram of steel containing not more than 0.15 mg. of chromium in 4 ml. of concentrated sulfuric acid and 25 ml. of water. To the hot solution, add, cautiously, 1 ml.

[86] Selected from the literature by the editor.
[87] Willard and Thompson, Ind. Eng. Chem., Anal. Ed., **3**, 399 (1931).

or more of concentrated nitric acid to oxidize the ferrous iron and carbonaceous matter, and boil to remove nitrous fumes. Any graphite present will do no harm and will be filtered out later. Dilute to 50 or 75 ml., add 3 ml. of 85% phosphoric acid (or an equivalent amount of more dilute acid) and 0.3 gram of sodium or potassium periodate. Boil gently for 15 minutes to oxidize the manganese, dilute to 150 ml., cool to room temperature, and add slowly, with constant stirring, 4 or 5 grams of mercuric nitrate ($Hg(NO_3)_2 \cdot 2H_2O$) dissolved in a little water. Filter immediately through a fairly large asbestos filter into an excess of standard ferrous sulfate, wash with cold water four or five times, and titrate back with standard permanganate.

Procedure for Steel or Iron Containing Not Over 0.1% of Chromium.—Dissolve 1 gram in a mixture of 15 ml. of water and 15 ml. of 85% phosphoric acid. Oxidize the ferrous iron and carbonaceous matter by adding carefully to the hot solution 1 or 2 ml. of concentrated nitric acid, and boil to remove nitrous fumes. Dilute to 100 ml., add 0.3 gram of sodium or potassium periodate, boil gently 15 minutes to oxidize the manganese, dilute to 150 ml., and cool to room temperature. Precipitate the periodate by adding slowly, with constant stirring, 2 to 3 grams of mercuric nitrate dissolved in a little water, and filter immediately through a fairly large asbestos filter into excess of standard ferrous sulfate containing 10 ml. of 50% sulfuric acid to prevent precipitation of mercuric phosphate. Wash with cold water four or five times and titrate back the filtrate and washings with standard permanganate. The filtration will be slower than when sulfuric acid is present during precipitation, but the time required, including washing, should not be more than 3 minutes.

Procedure for Iron Ore and Other Oxide Ores.—Place 1 gram in a 250 ml. Pyrex beaker, and add 15 ml. of 85% phosphoric acid and a few drops of concentrated sulfuric acid. Stir until all the ore is free from the bottom of the beaker, cover, and heat until fumes of sulfuric acid are given off, taking care that it does not froth over or cake on the bottom. If the ore is not dissolved by this time, keep it hot for a longer time, stirring occasionally, but not allowing the temperature to rise, because the beaker would be attacked. Cool until the mass begins to be viscous, then add quickly 100 ml. of water, and heat. Everything should dissolve except some gelatinous silica. From here on the procedure is the same as for steel containing 0.1% of chromium.

Procedure for Bronze.—Dissolve 1 gram in a mixture of 3 ml. of concentrated nitric acid, 10 ml. of 85% phosphoric acid, and about 7 or 8 ml. of water. Then dilute to 50 or 75 ml. and proceed as above. Owing to the deep blue color of the copper salt, the back titration with permanganate is conveniently carried out electrometrically or by use of alphazurine indicator.

NOTE.—If the amount of manganese is between 15 and 30 mg., the amount of periodate in the above procedures should be increased to 0.5 gram.

A MODIFIED PERSULFATE–ARSENITE METHOD FOR MANGANESE [88]

The permanganic acid formed by the oxidation of the sample with ammonium persulfate, in the presence of phosphoric acid with silver as catalyst, is

[88] E. B. Sandell, I. M. Kolthoff, and J. J. Lingane, Ind. and Eng. Chem., Anal. Ed., 7, 256, July 15, 1935.

titrated with a reducing solution containing equivalent amounts of sodium arsenite and sodium nitrite instead of with the customary sodium arsenite alone. With the mixed reducing solution, heptavalent manganese is reduced to the divalent condition, and the solution therefore becomes colorless at the end point instead of yellow or brown as when arsenite alone is used for the titration. Small amounts of chromium, vanadium, nickel, and molybdenum do not interfere. Silver must be precipitated as the chloride before the titration can be made.

Procedure for Manganese in Steels. ***Reagents.***—(1) Acid mixture (recommended by Bright and Larrabee): Water, 525 ml.; sulfuric acid, concentrated (sp.gr.=1.84), 100 ml.; phosphoric acid, 85%, 125 ml.; and nitric acid, concentration (sp.gr.=1.42), 250 ml. First add the sulfuric acid to the water, cool, and then add the nitric acid and phosphoric acids. (2) Silver nitrate solution, 0.1 M. (3) Ammonium persulfate solution, 25 grams (of 95% salt) in 80 ml. of water. Ammonium persulfate slowly decomposes in solution and therefore this solution should not be kept for more than 2 or 3 days. (4) Sodium chloride solution, 0.2 M. (5) Sulfuric acid, 12 N.

Standard Solutions.—(1) Sodium arsenite-sodium nitrite, 0.05 N. Dissolve 2.5 grams of pure arsenic trioxide in 25 ml. of 4 N sodium hydroxide solution, dilute to 200 ml., add slightly more than enough dilute sulfuric acid to neutralize the hydroxide, and then a slight excess of sodium bicarbonate to neutralize the acid (the solution should finally be neutral to litmus paper). Dissolve 0.85 gram of sodium nitrite in the solution thus obtained and dilute to 1 liter. (2) Potassium permanganate, 0.05 N. Prepare and standardize against pure dry sodium oxalate in the usual manner.

Standardization of Sodium Arsenite-Sodium Nitrite Solution.—Pipette 10 ml. of standardized 0.05 N potassium permanganate solution (for the best results the amount of permanganate taken should correspond approximately to the amount of manganese in the material under test) into a 250-ml. Erlenmeyer flask, and add 1.0 gram of electrolytic iron of known manganese content and 30 ml. of the sulfuric-phosphoric-nitric acid mixture. Warm to hasten solution, and finally boil for 2 to 3 minutes to expel oxides of nitrogen. Then add 50 ml. of cold water, 5 ml. of silver nitrate solution, and 10 ml. of ammonium persulfate solution. Heat to boiling, and boil for 30 to 45 seconds. Immediately cool the flask and its contents to 20° to 25° C. by placing in water. Add 5 ml. of sodium chloride solution and 10 ml. of 12 N sulfuric acid. Then titrate with arsenite-nitrite solution. Run in the reducing solution at a uniform rate not exceeding 5 or 6 ml. per minute, swirling the liquid in the flask continuously until the solution has become pale pink, and then continue the addition more slowly, allowing 5 seconds between drops. When very near the end point as indicated by the very pale pink color, allow approximately 10 seconds between drops or fractions of a drop. This slow addition is required only for the last few drops. The end point is reached when the color changes abruptly to white (suspended silver chloride). If the titration has been correctly performed, a drop of 0.05 N permanganate solution added after the end point has been reached will give a coloration persisting for at least 3 minutes.

Determination.—Dissolve a 0.9- to 1.1-gram sample of steel in 30 ml. of the acid mixture and then proceed as directed in the standardization (beginning with the second sentence).

NOTES.—If an accuracy greater than 0.01% of manganese is not required, the addition of iron in the standardization may be omitted. Then standardize as follows:

Transfer 30 ml. of acid mixture to a 250-ml. Erlenmeyer flask and add 50 ml. of water, 5 ml. of silver nitrate solution, and 10 ml. of ammonium persulfate solution. Boil for one minute, cool to room temperature, add 10 ml. of 0.05 N standard potassium permanganate, precipitate the silver, and titrate with the arsenite-nitrite solution as described above.

An equivalent amount of pure ferrous or ferric sulfate (but not ferrous ammonium sulfate or ferric alum) as free as possible from manganese, may be used instead of electrolytic iron in the standardization. In any case the manganese content of the iron or iron salt added must be determined colorimetrically, preferably with periodate as reagent (7, 8), and a correction applied if necessary.

When the manganese content of the sample falls outside the range 0.3 to 0.8% (using a 1-gram sample) the arsenite-nitrite solution should be standardized against a volume of standard potassium permanganate that contains roughly the same quantity of manganese as the sample. No more than 15 mg. of manganese may be present in the solution when diluted to 100 ml. previous to titration. In other words, using a 1-gram sample, not more than 1.5% of manganese may be present in the material analyzed if the above directions are to be followed.

Cast irons may be analyzed by the above procedure if the graphite, left after dissolving the sample, is filtered off before the oxidation.

CHROMIUM AND VANADIUM [89]

INDICATOR METHODS

Preparation of Indicator.—A 0.01 M solution of diphenylamine sodium sulfonate is prepared by dissolving 3.2 grams of the barium salt (obtainable from the Eastman Kodak Co., Rochester, N. Y.) in a liter of water, adding to this solution a slight excess of sodium sulfate, and decanting or filtering the solution.

Preparation of Oxidized Indicator.—The volume of the 0.01 M indicator solution specified in a given experiment is placed in a small beaker, 5 ml. of water, 3 or 4 drops of concentrated sulfuric acid, and 3 or 4 drops of 0.1 N potassium dichromate are added, and then very dilute ferrous sulfate (0.01 to 0.02 N) is added until the purple color, which appears on the addition of the first few drops of ferrous sulfate, just turns to a bluish green. As this purple color begins to disappear, the ferrous sulfate should be added in parts of a drop, in order to have no excess present in the oxidized indicator solution. This bluish green solution is added to the solution to be titrated. In the experiments described in this paper the oxidized indicator was prepared in separate samples for each titration.

A stock solution of the oxidized indicator is often more convenient and may be prepared as follows:

One hundred milliliters of 0.01 M diphenylamine sodium sulfonate and 25 ml. of concentrated sulfuric acid are diluted to 900 ml. in a liter volumetric flask. To this solution 25 ml. of 0.1 N potassium dichromate are added slowly with frequent shaking, followed by 0.1 N ferrous sulfate with repeated shaking, until one drop causes a visible change in color from bluish green to a clear deep green in the liquid when viewed through the neck of the flask. This will require approximately 6.5 ml. of ferrous sulfate.

Standardization of Ferrous Sulfate Solution for Vanadium Determinations.—Weigh out 0.04 to 0.06 gram samples of pure potassium dichromate into

[89] Willard and Young, Ind. and Eng. Chem., Anal. Ed., 5, pp. 154, 158 (1933).

400 ml. beakers and dissolve in a little water, or measure out that volume of standard dichromate solution which will require 35 to 50 ml. of 0.025 N ferrous sulfate for titration. Add 5 ml. of sulfuric acid (sp.gr. 1.5), 5 ml. of phosphoric acid (sp.gr. 1.37), and dilute to 200 ml. Then add 0.3 ml. of 0.01 M indicator, oxidized, and titrate with approximately 0.025 N ferrous sulfate. No blank correction is required in this standardization.[90]

Procedure for Vanadium in Tungsten Steels.—Add 25 to 30 ml. of water and 5 ml. of sulfuric acid (sp.gr. 1.83) to a 1-gram sample of the steel weighed into a 400-ml. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. Rub loose from the beaker all tungsten and to the boiling hot solution add 5 ml. of hydrofluoric acid (48%), then nitric acid (sp.gr. 1.42), at first slowly, using 5 ml. in all. Boil 2 minutes. A clear green solution is obtained. If the solution is not perfectly clear at this point, as occasionally happens with steels especially difficult to decompose, boil 2 or 3 minutes longer. Dilute to approximately 100 ml., add 1 gram of ammonium persulfate, and boil 5 minutes. Add 5 ml. of 0.1 N ferrous sulfate, dilute to between 175 and 200 ml., and cool to room temperature. Add to this solution 0.1 N potassium permanganate from a buret until a distinct color persists for 2 minutes, to be sure all the vanadium is oxidized. At this point either procedure *A* or *B* may be used. Procedure *A* is preferable.

A. Add 0.05 M sodium nitrite slowly from a buret until the solution becomes green, then 5 ml. excess of the nitrite solution, followed by 2 grams of urea. Stir the solution thoroughly and allow it to stand for 5 minutes.

B. Add 5 ml. of 0.1 M sodium azide and boil vigorously (in hood) for 5 minutes to remove all the hydrazoic acid. Cool to room temperature.

To the solution thus obtained add 3 ml. of hydrofluoric acid (48%) and 0.3 ml. of 0.01 M diphenylamine sodium sulfonate which has been oxidized, and titrate at once with 0.025 N ferrous sulfate standardized as directed below. The color change of the indicator at the end point is from purple to green. The correction to be applied for the indicator may be determined from the following table and should be subtracted from or added to the volume of ferrous sulfate used in the titration.[90]

Vanadium in Steel %	Indicator Corrections in 0.025 N $FeSO_4$ Ml.
0–0.85	−0.10
0.85–1.2	+0.05
1.2 –3.5	+0.10

Standardization of Ferrous Sulfate for Chromium Plus Vanadium Determinations.—Place in a 600 ml. beaker that amount of potassium dichromate, either in solid form dissolved in a little water or in the form of a standard solution, which will require approximately 35 to 50 ml. of 0.05 N ferrous sulfate. Add 5 ml. of sulfuric acid (sp.gr., 1.5), 5 ml. of phosphoric acid (sp.gr. 1.37) and dilute to 300 ml. Then add 0.3 ml. of 0.01 M indicator, oxidized, and titrate with approximately 0.05 N ferrous sulfate. No blank correction for the indicator is required here.

Procedure for Chromium Plus Vanadium in Tungsten Steels.—Add 25 to 30 ml. of water and 5 ml. of sulfuric acid (sp.gr. 1.83) to a 1-gram sample of the

[90] Willard and Young, Ind. Eng. Chem., Anal. Ed., 5, 154 (1933).

steel weighed into a 600-ml. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. Rub loose from the beaker all tungsten and to the boiling hot solution add 5 ml. of hydrofluoric acid (48%), then nitric acid (sp.gr. 1.42), at first slowly, using 5 ml. in all. Boil 2 minutes. A clear green solution is obtained. If the solution is not perfectly clear at this point, as occasionally happens with steels especially difficult to decompose, boil 2 or 3 minutes longer. Dilute to approximately 300 ml., heat to 60° C. or higher, add 10 ml. of silver nitrate solution (2.5 grams of silver nitrate per liter), 5 grams of ammonium persulfate, and boil vigorously for 10 minutes. A few small pieces of broken porcelain in the solution will prevent bumping. Any one of the three following procedures may be used to destroy the permanganic acid formed during the oxidation process. Procedure *A* is preferable.

A. Add 0.1 M sodium azide, drop by drop, from a pipette to the boiling hot solution until all permanganate has been reduced, limiting the excess of azide used to 1 or 2 drops. Boil for 1 or 2 minutes to remove the hydrazoic acid.

B. Add 0.05 M sodium nitrite, drop by drop, from a pipette to the boiling hot solution until all permanganate has been reduced, limiting the excess of nitrite used to 1 or 2 drops. Then add 1 gram of urea at once and stir the solution thoroughly.

C. Add 5 ml. of 1 to 3 hydrochloric acid to the hot solution and boil vigorously for 10 minutes to reduce the permanganate and remove all chlorine.

To the solution from *A*, *B*, or *C*, cooled to room temperature, add 3 ml. of hydrofluoric acid (48%) and 0.3 ml. of 0.01 M diphenylamine sodium sulfonate, oxidized, and titrate at once with 0.05 N ferrous sulfate standardized as directed below. Immediately after the addition of the indicator the solution is a yellowish brown. As the ferrous sulfate is added this yellow color disappears gradually, being replaced first by a purplish red and then by a clear purple. The color change at the end point from purple to green is very sharp. An indicator blank of −0.30 ml. of 0.05 N ferrous sulfate should be applied to the volume of ferrous sulfate used in the titration.

The usual procedures for determining chromium and vanadium in steels that do not contain tungsten may be carried out using oxidized diphenylamine as the indicator.

Preparation of Indicator.—A 1/10% solution of diphenylamine is prepared by dissolving 0.1 gram of the indicator in 10 ml. of sulfuric acid (sp.gr., 1.83) and diluting this solution with 90 ml. of glacial acetic acid. The method of preparing portions of oxidized indicator solution from the 0.1% solution is the same as used for diphenylamine sulfonic acid, except that 5 ml. of phosphoric acid (sp.gr., 1.37) instead of water are added to a measured volume of the indicator in a very small beaker. No sulfuric acid is added, but only 3 or 4 drops of dichromate, followed by very dilute ferrous sulfate.

Procedure for Vanadium in Steels without Tungsten.—Add 30 to 40 ml. of water to a 4- or 5-gram sample in a 600 ml. beaker. Run in a measured volume of sulfuric acid (sp.gr., 1.83) from a burette, allowing 1.5 ml. for each gram of steel and 3 ml. in excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 30 to 40 ml. of water and heat until the salts have dissolved. To the boiling hot solution add nitric acid (sp.gr., 1.42)

in small portions until the oxidation of ferrous sulfate is complete (3 to 5 ml. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen, cool to room temperature, add 25 ml. of phosphoric acid (sp.gr., 1.37), and dilute to 300 ml. Add 0.1 N potassium permanganate from a burette until an excess is present. Then add 3 or 4 drops more and let the solution stand for 2 minutes to be sure that the color persists and all of the vanadium is oxidized. Either procedure *A* or *B* may be used to destroy excess permanganate. Procedure *A* is preferable.

A. Add 0.05 M sodium nitrite slowly from a burette until the solution becomes green, then 5 ml. excess of the nitrite solution, followed by 2 grams of urea. Stir the solution thoroughly and allow it to stand for 5 minutes.

B. Add 5 ml. of 0.1 M sodium azide and boil vigorously (in hood) for 5 minutes to remove all hydrazoic acid. Cool to room temperature.

To the solution thus obtained, add 15 grams of crystallized sodium acetate. This should be the correct amount of acetate to react with the 3 ml. excess of sulfuric acid used in dissolving the steel and with the slight amount of nitric acid present. If too much acetate is added so that a permanent precipitate forms, a drop or two of sulfuric acid will cause the solution to clear. As soon as the acetate has dissolved, add 0.5 ml. of 0.1% diphenylamine, oxidized, and titrate with 0.025 N ferrous sulfate standardized by the method given below.

Standardization of Ferrous Sulfate Solution for Vanadium Determinations.—Use sufficient standard potassium dichromate solution to require 35 to 50 ml. of 0.025 N ferrous sulfate. Dilute to 300 ml., add 0.5 ml. of 0.1% diphenylamine, oxidized, and titrate with the 0.025 N ferrous sulfate.

Recommended Procedure for Chromium Plus Vanadium in Steels Without Tungsten.—Use a sample of suitable size, varying from 2 grams with low chromium to 0.25 gram with stainless steels. Place it in a 600 ml. beaker, add 15 ml. of water, 15 ml. of phosphoric acid (sp.gr., 1.37), and run in a measured volume of sulfuric acid (sp.gr., 1.83) from a burette. Allow 1.5 ml. of acid for each gram of steel and 3 ml. excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 ml. of water and heat until the salts have dissolved. Add nitric acid (sp.gr., 1.42) in small portions to the hot liquid until the violent oxidation of ferrous sulfate is over (2 to 3 ml. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen, dilute to 300 ml., heat to boiling and add 10 ml. of silver nitrate containing 2.5 grams of silver nitrate per liter, and 1.5 grams of ammonium persulfate. If no permanganate tinge appears in the solution on boiling add more ammonium persulfate. In no case will more than 2 to 2.5 grams be required if samples of the weights suggested above are used. Boil the solution for 10 minutes to decompose the excess persulfate, and use either procedure *A* or *B* to reduce the permanganate formed. *A* is preferable.

A. Add 0.1 M sodium azide, drop by drop, from a pipette to the boiling hot solution until all permanganate has been reduced, limiting the excess of azide added to 2 or 3 drops. Boil for 2 minutes to remove the hydrazoic acid. A reddish color which may develop in the solution during the boiling period may be disregarded.

B. Add 0.05 M sodium nitrite, drop by drop, from a pipette to the boiling hot solution until all permanganate has been reduced, limiting the excess used

to 2 or 3 drops. Then add 1 gram of urea at once and boil the solution for 5 minutes. A reddish color which may develop in the solution during the boiling period may be disregarded.

To the solution from *A* or *B*, cooled to room temperature, add that quantity of crystallized sodium acetate which is required to react with the excess of sulfuric acid used in dissolving the steel (1 ml. of concentrated sulfuric acid is equivalent to 4.8 grams of sodium acetate trihydrate). As soon as this has dissolved, add 0.5 ml. of 0.1% diphenylamine, oxidized, and titrate with 0.05 N ferrous sulfate. The ferrous sulfate should be standardized by the procedure given under vanadium in steels without tungsten. That volume of standard dichromate should be taken which will require about 35 to 50 ml. of ferrous sulfate.

Determinations of Chromium and Vanadium after Oxidation with Perchloric Acid [91]

Place samples of 0.5 to 2 grams, depending on the chromium content, in a 500-ml. tall-form lipped beaker, or better still in a 500-ml. Soxhlet flask, and add 20 to 25 ml. (depending on the size of the sample) of 70% perchloric acid, commercial or C.P. Cover the vessel and warm until all the metal has dissolved, taking care not to let the action become too violent. Most steels will dissolve in less than 5 minutes. Boil the solution 15 to 20 minutes, noting the change in color if much chromium is present, and continuing the boiling at least 10 minutes longer. The perchloric acid, should condense and run down the sides of the beaker or flask. Cool somewhat, add an equal volume of water, and boil 3 minutes to expel chlorine. After cooling, the solution is diluted to a suitable volume and is ready for titration as described later.

Cast iron or alloys high in carbon should be dissolved in dilute perchloric acid, either with or without nitric acid, and evaporated to fumes, because the action of the hot concentrated acid is too violent. If it is necessary to use 4- or 5-gram samples, add 50 or 60 ml. of acid. This is desirable in cast iron or steel very low in chromium. Boiling for 1 or 2 hours may be necessary to oxidize all the graphite, and further addition of perchloric acid may become necessary.

Procedure for Ferrochromium.—An alloy of this type requries different treatment, because when boiled with 70% perchloric acid, the chromium trioxide formed, which is fairly insoluble even in the hot acid, tends to coat the particles of ferrochromium and prevent further oxidation. Weigh 0.2 gram of the powdered alloy into a 500-ml. tall lipped beaker or Soxhlet flask. Add 20 ml. of hydrochloric acid, sp.gr. 1.18, and heat for 15 minutes. Add 15 ml. of 70% perchloric acid and boil 30 minutes after all hydrochloric acid is expelled. Cool somewhat, add a few cubic centimeters of water to dissolve the chromium trioxide and reoxidize by boiling 15 minutes after the water is expelled. Add a few cubic centimeters of water and look for any undissolved particles of metal. If any are present, another oxidation may dissolve them. Otherwise pour off most of the solution, add a few cubic centimeters of 70% perchloric acid to the residue, and boil till solution is complete. Add the main decanted liquid, evaporate off the water, and reoxidize for 5 minutes. Dilute and boil off chlorine.

[91] H. H. Willard and R. C. Gibson, Ind. Eng. Chem, Analyt. Ed., **3**, 88 (1931).

Procedure for Chromic Oxide and Chromite.—Chromic oxide, which is not attacked by the usual acids, is readily oxidized to chromic acid by boiling 70% perchloric acid, a 0.15-gram sample requiring 15 minutes. Chromite is more resistant; if ground to pass a 200-mesh sieve it requires 60–90 minutes.

Weigh a 0.5-gram sample into a tall, 500-ml. lipped beaker, or better still, Soxhlet flask. Add 20 ml. of 70% perchloric acid and boil 30 to 60 minutes. Cool somewhat, then add a few cubic centimeters of water to dissolve the chromium trioxide which coats the particles. If any unattacked ore remains, evaporate off the water and boil the concentrated acid again for 20 or 30 minutes. If this treatment does not decompose all the ore, pour off most of the solution, add to the residue 10 ml. of perchloric acid, and boil until the ore is dissolved. Add the main decanted solution, evaporate off the water, oxidize 5 minutes, dilute, and boil off the chlorine. The solution is diluted to a suitable volume and when cool, is ready for titration.

Titration of Chromic Acid.—After the chromium has been oxidized as already described, it may be titrated by any of the usual methods.

(1) Excess of standard ferrous sulfate is added and the excess is titrated back by means of standard permanganate, allowing 1 minute for the end point if vanadium is present. This method is so well known as to need no description. In the absence of vanadium, the end point is made much sharper by adding 0.5 ml. of a 0.1% solution of erioglaucine *A*, better known as alphazurine (Schultz 506) as recommended by Knop.[92] The change from green to red after the addition of an excess of 0.03 ml. of 0.1 N permanganate in 300 ml. if very distinct even in the presence of the chromic salt. The color lasts only a few seconds.

(2) Excess of standard arsenite is added, which is then back-titrated with permanganate in the presence of hydrochloric acid and a trace of iodide as catalyst, as described by Kolthoff and Sandell.[93] If vanadium is absent, alphazurine as indicator improves the end point. In testing this method 2-gram samples were used, phosphoric acid was not really necessary, and vanadium was determined in the same solution by titration with ferrous sulfate using diphenylbenzidine as indicator, following the directions of the authors. Good results were obtained. The amount of acetate to be added is discussed in connection with the next method.

(3) The chromic acid (and vanadic acid, too, if present) is titrated directly with standard ferrous sulfate either electrometrically in a strongly acid solution, or by the use of diphenylbenzidine as indicator in a solution containing phosphoric acid and sufficient sodium acetate to react with all the perchloric acid present, according to the method of Willard and Young.[94] The procedure is as follows: After boiling off the chlorine, cool, dilute the perchloric acid solution to 200 to 400 ml., add 15 ml. of phosphoric acid (sp.gr. 1.37) and, stirring constantly, a weight of sodium acetate trihydrate equivalent to the excess of perchloric acid used in dissolving the steel. One gram of iron was found to require about 5.4 ml. of 70% perchloric acid for conversion into ferric perchlorate, and 1 ml. of this acid contains 1.17 grams of perchloric acid, equivalent to 1.58 grams of crystallized sodium acetate. Thus, if 20 ml. of acid are added,

[92] Knop, Z., anal. Chem., **77**, 125 (1929).
[93] Kolthoff and Sandell, Ind. Eng. Chem., Anal. Ed., **2**, 140 (1930).
[94] Willard and Young, Ind. Eng. Chem., **20**, 764, 769 (1928).

the excess will require about 23 grams of acetate. If the steel was first dissolved in nitric acid, the excess of perchloric acid will be a little greater. The proper amount of acetate has been added when more would form a permanent white precipitate of ferric phosphate. If this occurs, add dilute sulfuric acid, with constant stirring, until the solution clears. Unless the acidity is reduced in this way, the color change at the end point will be slow. Add 0.6 to 0.8 ml. of 0.1% diphenylbenzidine solution (in phosphoric or acetic acid), and allow 5 minutes, but not more than 10, for the purple color to develop. It will appear brownish until most of the chromic acid is reduced. If no color appears, add a few drops of dilute sulfuric acid. Titrate with ferrous sulfate to a clear green, approaching the end point carefully. Add a correction of 0.04 ml. of 0.1 N ferrous sulfate for each 0.5 ml. of indicator.

For the electrometric method add 25 to 30 ml. of sulfuric acid (sp.gr. 1.5) and titrate chromic plus vanadic acids with ferrous sulfate. If much vanadium is present, a much sharper end point is obtained by cooling the solution to 5° C.

Whichever method is used, it has already been shown that the ferrous sulfate should be standardized in the same way and under the same conditions of volume and acidity at about the time it is used.

Titration of Vanadium.—This may be determined by any of the usual methods.

Silica has been dehydrated by the boiling perchloric acid and after the titration it may be filtered off and determined.[95]

Chromium and Vanadium in the Same Sample [96]

Procedure, Perchloric Acid Method.—Weigh a sample of suitable size, varying from 2 grams with low chromium to 0.25 gram with stainless steels, into a 500 ml. lipped beaker of tall form or into a 500 ml. Soxhlet flask. If the latter is used, the watch glass should be placed on very thin glass hooks or on a bent platinum wire about 1 mm. in diameter to prevent the formation of a liquid seal when the contents of the flask are heated. Add 20 to 25 ml. of 70% perchloric acid (depending on the size of the sample) and heat very slowly to prevent the reaction from becoming violent. After the steel has dissolved (usually only 3 to 5 minutes will be required) boil the solution for 15 to 20 minutes. The longer period is better for high-chromium steels. Cool the flask and contents a moment in the air and then in a stream of running water. Add 25 ml. of water, rinse off the watch cover into the beaker, and boil the solution for 3 minutes to remove all chlorine. Dilute the liquid to 250 to 300 ml. and cool in running water. If the steel contains more than a trace of vanadium so that two end points are to be determined in the titration with standard permanganate, 15 ml. of phosphoric acid (sp. gr., 1.37) are added most conveniently at this point. Add to the solution at room temperature a measured excess of 0.1 N ferrous sulfate, and then two or three drops of 0.025 M *o*-phenanthroline ferrous complex. Much of the indicator precipitates, but sufficient of it is dissolved for the first end point and all of it dissolves on heating the solution before the second titration is commenced.

Titrate immediately after the solution of the indicator with 0.05 N potassium permanganate until the color of the solution changes from pink to a clear

[95] Willard and Cake, J. Am. Chem. Soc., **42**, 2208 (1920).
[96] Willard and Young, Ind. Eng. Chem., Anal. Ed., **6**, 48 (1934).

green. The end point is very sharp and there is almost no return of the pink color for a minute or more. Add sufficient crystallized sodium acetate to react with the free perchloric acid present. The amount of this salt required may be estimated approximately by considering that 5.4 ml. of 70% perchloric acid are used to decompose and oxidize each gram of steel and that 1.6 grams of the acetate will be required for each cubic centimeter of the acid remaining. If preferred, the acetate may be added in small portions to the solution while it is being heated, until the addition of further acetate would cause the formation of a permanent precipitate of ferric phosphate. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl at once with the 0.05 N permanganate. The oxidizing agent should be added slowly, as only a small volume of it will be required and also because the reaction between vanadyl and permanganate ions is not instantaneous. The color change at the end point is the same as in the first titration and the end point is considered as reached when there is no return of a pale pink shade during an interval of a minute. It is sometimes advisable to add a drop more of indicator before titrating the vanadium.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 ml. of the permanganate to 250 ml. of water containing 10 to 15 ml. of 70% perchloric acid. Add 2 drops of 0.025 M *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

DETERMINATION OF SELENIUM IN STAINLESS STEELS [97]

Dissolve a 5 gram sample in 60 ml. of a mixture of equal parts of concentrated HNO_3 and concentrated HCl in a 500-ml. Erlenmeyer flask. The initial reaction is usually very rapid, and can be controlled by cooling the flask. After the initial reaction has subsided, solution of the sample is completed on the hot plate.

Add 35 ml. of 70% $HClO_4$ and evaporate to dense fumes, continue fuming until the condensation of the vapor is observed near the neck of the flask.

Cool, add 100 ml. of cold water and warm slightly to effect solution of salts. Filter through a No. 42 Whatman paper to remove silica, washing well with HCl (1 : 1) and hot water. The volume of the filtrate should be held to 150 to 175 ml.

Add 125 ml. concentrated HCl and 100 ml. water freshly saturated with SO_2. Heat to 70° C. and allow to stand at this temperature for three hours. A higher temperature tends to increase the contamination of the precipitated selenium by occlusion.

Cool to room temperature and filter the metallic selenium on a weighed Gooch crucible. The asbestos should be of the amphibole variety and should be thoroughly washed with warm HCl (1 : 1) and water freshly saturated with SO_2. After filter has been prepared, dry and ignite at 700° C., cool and weigh.

Filter the solution containing the selenium through the crucible, wash precipitate free of iron with warm dilute HCl (1 : 1). Wash free of acid with warm water, followed by two alcohol (96%) washing and one ether washing. Dry for one hour at 100° C. and weigh.

[97] Standard Procedure of the Carpenter Steel Co., Reading Pa., through the Courtesy of W. J. Boyer, Asst. Chief Chemist.

Record the gain in weight as "impure selenium." To check the purity, ignite to constant weight at a temperature of 700° C. If this weight is within 1.0 mg. of the ignited tare weight, and the asbestos mat shows no marked discoloration, consider the selenium pure. Otherwise, subtract the ignited weight of the crucible after volatilizing the selenium, and record the difference as pure selenium. Divide the weight of selenium by weight of sample taken, times 100, to calculate the per cent selenium.

NOTE.—This method runs on an average 0.02% higher as compared to the volumetric procedures recently published.[98]

THE RAPID DETERMINATION OF MOLYBDENUM IN STEEL[99]

Solutions Necessary. *Hydrochloric-sulfuric Acid Mixture.*—H_2O, 1450 ml., H_2SO_4, sp. gr. 1.84, 450 ml., HCl, sp. gr. 1.19, 100 ml.

Nitric-sulfuric Acid Mixture.—H_2O, 750 ml., HNO_3, sp. gr. 1.42, 350 ml., H_2SO_4, sp. gr. 1.84, 225 ml.

Potassium Sulfocyanate Solution.—KCNS, 50 grams, H_2O, 1000 ml.

Stannous Chloride Solution.—$SnCl_2$, 250 grams, HCl, sp. gr. 1.19, 200 ml., H_2O, 800 ml. Dissolve the stannous chloride in the hydrochloric acid, boil until clear, and add the water. Add a few pieces of metallic tin to prevent oxidation.

Procedure.—Weigh a 0.5-gram sample of steel and place in a 400 ml. beaker. Add 10 ml. of nitric-sulfuric acid mixture. Heat gently until the sample is in solution, then evaporate carefully and rapidly on a hot plate to copious fumes. Do not use a cover glass. Some trouble due to spattering may be experienced at first; however, a little practice in regulating the temperature of the hot plate will readily overcome this difficulty. To obtain concordant results all nitrates must be driven off, which necessitates steady fuming.

Cool the contents of the beaker; add exactly 30 ml. of hydrochloric-sulfuric acid mixture and heat until the salts dissolve. The amount of hydrochloric acid used in this operation is very important; too much will cause a fading of the color even before the ether extraction can be made, while not enough of this reagent may present difficulties in the solution of the salts. Then add 30 ml. H_2O.

Cool the solution to room temperature; add from a burette 5 ml. of potassium sulfocyanate solution. Stir well and add 10 ml. of stannous chloride solution from a burette and again stir thoroughly. It is very important that all of the iron be reduced before the extraction is made; therefore, after the addition of the stannous chloride care should be taken that none of the unreduced solution is left on the sides of the beaker.

Extraction with Ether.—Transfer the acid solution to a separatory funnel of suitable size; add 20 ml. of ether and shake well. Return the acid solution

[98] Determination of Selenium in 18–8 Stainless Steels, by G. G. Marvin, with W. C. Schumb. Ind. & Eng. Chem., Anal. Ed., 8, 109 (1936). Determination of Selenium in Steel, by W. C. Coleman and C. R. McCrosky. Ind. & Eng. Chem., Anal. Ed., 8, 196 (1936). Gravimetric Determination of Selenium in Alloy Steels, by Louis Silverman. Ind. & Eng. Chem., Anal. Ed., 8, 132 (1936).

[99] By O. L. Maag and C. H. McCollan, The Timken Steel & Tube Company, Canton, Ohio, Ind. Eng. Chem., **17**, 524 (1925).

to the original beaker and draw off the ether solution into a clean, dry 50 ml. graduated cylinder. Shake out the acid mixture with successive 10 ml. portions of ether until all color is removed, if one extraction does not remove same. The volume of ether used for the sample should be approximately the same as is required to give a corresponding color with the standard. Transfer the combined ether solutions to a graduated matching tube.

Color Comparison.—For this operation a Kennicott-Campbell Hurley colorimeter may be used. Illumination is supplied by a Wratten Safelight No. 2, made especially for dark-room purposes. This fixture carried a 50 watt bulb, which gives sufficient light and does not materially affect the atmospheric temperature and thus cause a rapid deterioration of the standard due to evaporation of the ether. It is essential that the light be so placed that the illumination is equal on both mirrors.

Place the matching tube containing the unknown in the colorimeter, and adjust the leveling device until the depth of color in the tube containing the standard equals that of the unknown. Take the reading in milliliters of the standard solution in the graduated matching tube. From this value the molybdenum content of the unknown steel can be calculated.

Standard Solution.—Weigh two 0.5-gram samples of standard steel. Run through in the usual manner and make the ether extract up to exactly 50 ml. in the standard matching tube. Place in the colorimeter and compare. If the color tints match, one sample may be diluted to exactly 100 ml. as a standard for low percentage molybdenum, or the two may be united to make a standard for steels with a higher molybdenum content. Transfer to the leveling tube of the colorimeter.

The top of the leveling tube should be covered when not in use, in order to increase the time that a standard can be used. Since the deterioration of a standard is generally due to evaporation of the ether rather than breaking down of the salt, its life is largely dependent on the room temperature. In this laboratory the standard is renewed every two hours, two samples of standard steel being kept fuming slightly on the cooler portion of the hot plate, to be used whenever the standard in use is suspected.

Calculation of Results.—If a steel containing 0.23% molybdenum is used as a standard, a 1-gram sample will contain 0.0023 gram of molybdenum; on dilution to 100 ml. each cubic centimeter will contain 0.000023 gram of molybdenum. If 14 ml. of the standard are used to match the color of the unknown steel, the unknown must contain 14×0.000023, or 0.000322 gram.

Since the weight of the unknown used is 0.5-gram, it will contain twice this amount per gram, or 0.064%.

$$\frac{\text{Ml. standard (14)} \times \text{grams/ml. (0.000023)}}{\text{Grams sample (0.5)}} = \%\ \text{Mo (0.064)}.$$

ELECTROLYTIC DETERMINATION OF TITANIUM, ZIRCONIUM OR ALUMINUM IN CHROMIUM STEELS AND ALLOYS [100]

The practice of adding 0.5 to 3% titanium or zirconium to " Enduro " and other high chromium alloys during the last few years has created a demand for

[100] By H. A. Kar, Research Chemist, The Timken Steel & Tube Co., Canton, Ohio, Metals and Alloys, (1935).

a short and accurate method for determining the exact amount of these elements held in the steel. By electrolysis the interfering elements are deposited while titanium, zirconium and aluminum, if present are left in the solution.

Apparatus.—The mercury in this method is used as the cathode and the power is supplied by a 1/16-in. thick platinum wire sealed in a glass tubing. About ½ in. of the platinum wire is left outside the lower end of the sealed glass tube to be dipped in the mercury from the side of the beaker and about 2 in. above the upper end of the glass tubing to be connected to the negative pole of the circuit.

A platinum plate, about 1¼ in. in diameter, welded to a ⅛-in. thick platinum wire and sealed in a glass tube, is used as the anode. The anode is connected to the positive pole of the circuit, and lowered about ½ in. below the surface of the solution. The plate is provided with a hole about ⅜ in. diameter in the center for the stirring rod.

The mercury is constantly agitated during electrolysis by a " T "-shaped glass rod passing through the hole in the plate and attached to a motor driven stirrer. The " T " end of the rod reaches the bottom of the mercury and is adjusted to operate without touching the beaker or electrodes.

Procedure.—Transfer one gram sample (two grams if titanium is less than 0.5%) to a 200-ml. beaker, add 20 to 40 ml. of 10% sulfuric acid, and heat slowly until action is complete. Filter into a 200 ml. tall electrolytic beaker containing mercury about one inch deep, wash a few times with water, and reserve the paper. The filtrate and washing should not exceed 75 ml. in volume

Set the beaker containing the solution in a trough of circulating water and electrolyze at 4 amp. for 1½ to 2 hrs. As soon as electrolysis begins, transfer the reserve filter paper to a platinum crucible and ignite. Cool, add a little potassium bisulfate and fuse. Add 5 ml. water and 3 drops of sulfuric acid in the crucible and heat to dissolve the melt. Cool and combine with the main solution.

At the end of a set period, withdraw a drop of the electrolyte and treat with a drop of fresh 1% solution of potassium ferrocyanide; if a blue color does not develop, raise the electrodes above the surface of the electrolyte and wash with cold water. Shut off the power and get the beaker out of the water trough. Filter, wash about 5 times with cold ½% sulfuric acid and proceed with the filtrate by either of the following two methods.

1. Add enough sulfuric acid to the filtrate to make it 10% acid by volume, cool and treat slowly with 6% solution of cupferron while stirring, until furthr addition does not cause a precipitate. Allow this to settle for 5 min. Filter on suction and wash 5 times with 10% cold hydrochloric acid and 10 times with cold water. Transfer the paper to a platinum crucible, dry and ignite. Volatilize the silica with hydrofluoric acid in the presence of sulfuric acid and again ignite at 1000° C. in an electric muffle for one-half hour. Cool and weigh.

2. Treat the filtrate with excess of ammonia, add a couple of crystals of ammonium persulfate and boil for 2 min. Add paper pulp in the beaker and stir. Filter and wash with ammoniacal hot water. Transfer the paper to a platinum crucible and ignite. Volatilize the silica with hydrofluoric and sulfuric acid and ignite at 1000° C. in an electric muffle for ½ hr. Cool and weigh.

Fuse the residue left in the crucible with a little potassium bisulfate, cool the melt and dissolve in 20 ml. of 20% sulfuric acid. Transfer the solution to a 200-ml. beaker, add 2 grams of citric acid, and stir to dissolve. Render the solution decidedly alkaline with ammonia and saturate for 5 min. with H_2S. Filter and wash 10 times with 5% ammonium citrate saturated with ammonium sulfide. Transfer the paper to a crucible and ignite. Cool and weigh. The difference in weight is titanium or zirconium oxide. If titanium is sought multiply by 60, and if zirconium is sought multiply the weight of oxide by 73.9.

This method can be applied to all kinds of steel alloyed with titanium or zirconium.

Determination of aluminum in nitralloy or other aluminum alloy steels is made by this method, proceeding exactly as described above and precipitating aluminum by ammonia after iron, chromium and other interfering elements are deposited.

The determinations of titanium and zirconium in ferrotitanium and ferrozirconium are also made by this method, precipitating either one by cupferron after electrolysis is completed.

This procedure works well for uranium in steels, if vanadium is absent. Mercury does not deposit the vanadium as it does the iron, manganese, chromium, cobalt, nickel, molybdenum, tin and copper.

The mercury can be cleaned and used again after every determination either by shaking it in a separatory funnel with concentrated hydrochloric acid, or pressing through a chamois skin.

ALLOYS, III

FERRO-ALLOYS

TENTATIVE METHODS OF CHEMICAL ANALYSIS OF FERRO-ALLOYS [1]

A. S. T. M. Designation: A 104–36 T [2]

FERROSILICON

Determination of Silicon by Fusion with Sodium Peroxide and Dehydration with Hydrochloric Acid

Transfer 0.5000 g. (use 0.4000 g. for 90% silicon) of the finely powdered sample (passing a No. 150 sieve [3]) to a 50-ml. pure iron crucible made from No. 20 gage (0.32 in. thickness) ingot iron, add approximately 10 g. of sodium peroxide. Mix *thoroughly* with a platinum or iron rod and carefully clean the rod of adhering particles by scraping with another rod. Cover the mixture with a layer of about 2 g. of additional peroxide. Heat the crucible and contents on a hot plate for 5 to 10 minutes to expel any water in the peroxide which would cause spattering in the subsequent fusion. Carefully fuse over a low flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down quietly. When the fusion is molten rotate the crucible carefully to stir up any unattacked particles on the bottom or sides, the crucible and contents being maintained at a low red heat. Just before completion of the fusion, which requires only three or four minutes, increase the temperature to bright redness for a minute. If the reaction has proceeded too violently, due to too rapid heating, to the use of insufficient sodium peroxide, or to the lack of thorough mixing, appreciable loss will occur and the work should be repeated.

Cover the crucible and allow it to cool until the fusion has solidified, and tap the crucible, while still warm, several times on an iron plate, which will loosen the fused mass in a solid cake. When the crucible and cake have completely cooled, transfer the cake to a large (275-ml.) gold or preferably platinum dish. Cover the dish with a clock glass and cautiously add 50 ml. of cold water.

[1] Under the standardization procedure of the Society, these methods are under the jurisdiction of the A. S. T. M. Committee E-3 on Chemical Analysis of Metals. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St. Philadelphia, Pa.

[2] This is a *Tentative Standard* and under the Regulations of the Society is subject to annual revision. Suggestions for revision should be addressed to the Headquarters of the Society, 260 S. Broad St., Philadelphia, Pa. Issued as Tentative, 1925; Adopted, 1927; Revised, 1934; Reverted to Tentative, 1936.

[3] For detailed specifications for this sieve, see Standard Specifications for Sieves for Testing Purposes (A. S. T. M. Designation: E 11) of the American Society for Testing Materials, 1936 Book of A. S. T. M. Standards, Part II, p. 1413.

When the reaction ceases, wash the small amount of adhering matter in the crucible into the dish with a little water. Cool the solution and carefully add an excess of hydrochloric acid. Evaporate to dryness, preferably on a steam bath, but do not bake at a temperature above 110° C. If platinum or gold dishes are not available for solution of the fused cake, the latter can be disintegrated with water in a pure nickel dish and the contents then transferred to a porcelain dish containing sufficient hydrochloric acid to provide an excess of acid. It is not desirable to dissolve the fusions directly in porcelain, because of the action of the alkaline solution.

When the residue is dry, allow the dish to cool. Add 10 ml. of hydrochloric acid (sp.gr. 1.13), cover the dish and heat gently for a few minutes. Dilute with 100 ml. of hot water, digest for a few minutes and filter through an 11-cm. paper. Wash about eight times with hot 5% hydrochloric acid, three times with warm 5% sulfuric acid and a few times with hot water. Reserve this paper until the second evaporation has been completed.

Evaporate the filtrate to dryness and bake the covered casserole or dish at 110° C. for one hour. Heating at a higher temperature is unnecessary and also disadvantageous. Cool, add 10 ml. of hydrochloric acid (1 : 1), digest on the steam bath for ten minutes, add 100 ml. of warm water, filter immediately and wash about eight times with cold 1% hydrochloric acid, twice with cold 5% sulfuric acid and a few times with cold water.

Place the paper and silica from the *second* dehydration in a large partially covered platinum crucible and char the paper without inflaming. Add the paper containing the silica from the first dehydration, char as before and then ignite carefully until the carbon has been burned off. Great care should be exercised in igniting the papers as the current of air produced by a burning filter is sufficient to carry finely divided silica out of the crucible. When the carbon of the filter paper has been completely burned, gradually heat the tightly covered crucible in a muffle at 1100° to 1125° C. for 30 minutes. Cool in a desiccator, weigh and check for constant weight by ten minutes additional heating at the above temperature. Add sufficient sulfuric acid (1 : 1) to moisten the silica and then 15 to 20 ml. of pure hydrofluoric acid (48%). Evaporate to dryness, ignite and weigh. The loss represents silica which contains 46.72% of silicon. A blank, not omitting the same amount of hydrofluoric acid, should be carried through all stages of the operation.

Note.—The silica remaining in the filtrate after the second dehydration is practically negligible, averaging about 0.0006 to 0.0010 g. in hydrochloric dehydration and 0.0010 to 0.0015 g. in sulfuric dehydration.

FERROMANGANESE

Determination of Manganese by the Modified Bismuthate Method [4]

Reagents Required: ***Dilute Nitric Acid*** ***(sp.gr. 1.135)***.—Mix 280 ml. of nitric acid (sp.gr. 1.42) and 720 ml. of distilled water. Test for proper specific gravity.

Dilute Nitric Acid ***(3 : 97)***.—Mix 30 ml. of recently boiled nitric acid (sp.gr. 1.42) and 970 ml. of distilled water. Add a little sodium bismuthate and shake well.

[4] J. of Ind. Eng. Chemistry, **16**, 58 (1924).

Asbestos.—Asbestos for this work should be digested in hot nitric acid (sp.gr. 1.42) and then washed free from acid with distilled water.

Sodium Bismuthate.—This reagent should be of 80% grade and its oxidizing power tested as follows: Shake 0.5 g. of the reagent with 4 g. of potassium iodide and a little water in a stoppered flask. Add 15 ml. of hydrochloric acid and allow to stand in the dark, with occasional shaking until the bismuthate has entirely decomposed. Dilute to 300 ml. and titrate with 0.1 N sodium thiosulfate, using starch as an indicator at the end. One milliliter of 0.1 N $Na_2S_2O_3$ equals 0.0140 g. of $NaBiO_3$.

Standard Potassium Permanganate Solution.—See the Determination of Chromium in Ferrochromium.[5] One milliliter of 0.1 N $KMnO_4$ equals 0.001099 g. of manganese.

Method: (*A*) *Solution of the Sample.*—All samples should be crushed to approximately a size to pass a No. 100 sieve and dried at 105° to 110° C.

With high-carbon 80% ferromanganese, dissolve 0.25 g. of the prepared sample in 60 ml. of nitric acid (sp.gr. 1.42) in a 750-ml. Erlenmeyer flask, provided with a clock-glass cover or trap to prevent loss by spraying.

Add 2 g. of potassium nitrate and boil gently until the volume of the solution has been reduced to about 15 ml. Cool, add 10 ml. of H_2SO_4 (1 : 1) and evaporate to strong fumes of sulfuric acid. Cool somewhat, dilute the solution with 200 ml. of HNO_3 (sp.gr. 1.135), heat to boiling, remove from the heat and add sodium bismuthate a little at a time until a precipitate of manganese dioxide has formed. When this occurs, add sulfurous acid dropwise until the precipitate has dissolved and an excess of about 1 ml. has been provided to reduce any chromium to the trivalent form. Boil the solution about five minutes to completely expel oxides of nitrogen, dilute to 250 ml. with water, cool the flask and solution in crushed ice and treat as described later. High-carbon ferromanganese containing 1% or more of chromium may not dissolve completely in nitric acid. In this case, dilute the solution after treatment with nitric acid, filter, and fuse the washed residue with a little sodium carbonate. Dissolve the melt in a small volume of nitric acid (sp.gr. 1.135), and add it to the main solution. Treat with potassium nitrate, etc., as previously described.

With low-carbon ferromanganese or manganese metal dissolve 0.2500 g. of the sample in 250 ml. of nitric acid (sp.gr. 1.135) in a covered 750-ml. Erlenmeyer flask and boil the solution gently for a few minutes to expel oxides of nitrogen. Treat with bismuthate and sulfurous acid as described above.

With silico-manganese (60 to 70% of manganese) and manganese-silicon (20 to 25% of manganese) treat 0.3000 g. of the former and 1.000 g. of the latter with 5 ml. of hydrofluoric acid in a large platinum dish equipped with a gold or platinum cover. (Some spiegeleisens are completely soluble in nitric acid in which case the sample can be dissolved directly in 250 ml. of nitric acid (sp.gr. 1.135). When the reaction moderates, add nitric acid (sp.gr. 1.42) a few drops at a time until the sample has completely dissolved. Add 10 ml. of nitric acid ((sp.gr. 1.42) and evaporate to a syrupy consistency. Again add 10 ml. of nitric acid (sp.gr. 1.42) and evaporate as before to expel hydrofluoric acid. Dissolve the residue in nitric acid (sp.gr. 1.135), transfer to a 750-ml. Erlenmeyer flask, dilute with nitric acid (sp.gr. 1.135) to 250 ml. and treat as described before with sodium bismuthate, etc.

[5] See p. 1490.

(*B*) ***Oxidation of Manganese.***—If the preceding directions have been followed, the manganese will be present in a concentration of approximately 0.001 g. per 1 ml. of nitric acid (sp.gr. 1.135). This concentration of manganese and nitric acid, together with a temperature of 10 to 15° C. are the conditions which insure maximum stability of the permanganic acid, formed as further described. To insure complete oxidation of the manganese to permanganic acid, it is essential that the sodium bismuthate (80% of $NaBiO_3$) be used in the ratio of at least 26 g. to every gram of manganese in solution. Add approximately 7.0 g. of sodium bismuthate (80%) to the flask, *agitate briskly* for one minute, dilute with 250 ml. of cold water, and filter immediately on a layer of acid-washed asbestos supported on a 2-in. alundum or perforated porcelain plate resting in a large glass funnel. The filter can be washed free from manganese more readily if not allowed to run dry during the filtering and washing. Wash the filter and residue with cold 3% nitric acid until the washings are entirely colorless and immediately treat the filtrate and washings as described in the following paragraph.

Weigh accurately 9.000 g. of ferrous ammonium sulfate, taken from a bottle of the well-mixed salt, and add to the filtered solution of permanganic acid. Stir briskly and as soon as the reduction is complete and the salt has dissolved, titrate the excess of ferrous salt with 0.1 N potassium permanganate. The manganese value of the ferrous salt is obtained in the following manner:

Two hundred and fifty milliliters of nitric acid (sp.gr. 1.135) contained in a 750-ml. Erlenmeyer flask are treated with approximately 2.0 g. of sodium bismuthate and the solution is vigorously agitated for one minute, diluted with 250 ml. of cold water, and immediately filtered on a layer of acid-washed asbestos as previously described. Five (5.0000) grams of the ferrous ammonium sulfate are added to the filtrate and the resulting solution is immediately titrated with 0.1 N $KMnO_4$ until a faint pink color appears. The excess of permanganate used to cause an end point color must be determined by watching the color in another beaker containing the same amounts of acid and cold water.

Notes.—1. Chromium when less than 2% does not cause any interference if the reactions are rapidly done in cold solutions. Larger amounts interfere to some extent and should be separated prior to the final oxidation with bismuthate.

2. The gravimetric determination of manganese by the pyrophosphate method will give high values if the precipitate of manganese ammonium phosphate is allowed to stand more than ten hours before filtration.

3. Volumetric methods such as Volhard's, Ford-Williams' and Julian's do not permit the use of a theoretical titre. Each necessitates the use of an empirical titre obtained by titration of material of known manganese content which has been carried through all steps of the method.

Determination of Carbon by the Direct-Combustion Method

See the Determination of Carbon in Ferrochromium by the Direct-Combustion Method.[6] A furnace temperature of 1150° to 1175° C. suffices, and high-silicon material should be covered with 1 or 2 g. of ingot iron.

Determination of Phosphorus by the Alkalimetric Method

Solutions Required: ***Dilute Nitric Acid (sp.gr. 1.135).***—Mix 280 ml. of HNO_3 (sp.gr. 1.42) and 720 ml. of distilled water.

[6] See p. 1493.

Ammonium Molybdate.—See the Determination of Phosphorus in Ferrovanadium by the Modified Molybdate-Magnesia Method.[7]

Standard Sodium Hydroxide.—Dissolve 6.5 g. of purified NaOH in 1000 ml. of distilled water, add a slight excess of a 1% solution of $Ba(OH)_2$, let stand for 24 hours, decant the liquid and standardize against Bureau of Standards Standard Benzoic Acid as follows: Dissolve 0.6 g. of benzoic acid in 15 ml. of alcohol in a small Erlenmeyer flask and titrate in the cold with phenolphthalein indicator, taking precautions to prevent access of carbon dioxide from the air during titration. The ratio of phosphorus to sodium hydroxide is taken as 1 to 23 in calculating the value of the sodium hydroxide. Protect the solution from carbon dioxide with a soda-lime tube.

Standard Nitric Acid.—Mix 10 ml. of HNO_3 (sp.gr. 1.42) and 1000 ml. of distilled water. Titrate the solution against the standard hydroxide solution, using phenolphthalein as an indicator. Adjust the solution so that it is equivalent to the sodium hydroxide solution.

Dilute Ammonium Hydroxide (sp.gr. 0.96).—Dilute 400 ml. of NH_4OH (sp.gr. 0.90) with 600 ml. of water. The strength of this solution should be established by titration or test with a hydrometer.

Method.—Dissolve 2.000 g. of the sample in 70 ml. of nitric acid (sp.gr. 1.42), evaporate to dryness and bake for two or three hours at 120° C. High-silicon alloys may require the addition of a little hydrofluoric acid for complete decomposition. In this case, several evaporations with 15 ml. portions of nitric acid (sp.gr. 1.42) should be made to remove hydrofluoric acid before the baking treatment. Moisten the residue with 25 ml. of dilute hydrochloric acid (1 : 1), digest a few minutes,[8] add 75 ml. of water, heat until the salts are dissolved and then filter to remove silica. Evaporate the filtrate to a syrupy condition, add 15 ml. of nitric acid (sp.gr. 1.42) and again evaporate to a small volume. Again add 15 ml. of nitric acid (sp.gr. 1.42) and evaporate to a small volume. Add 100 ml. of nitric acid (sp.gr. 1.135), heat to boiling and add a 1.5% solution of potassium permanganate until oxides of manganese are precipitated. Dissolve the oxides of manganese by addition of sulfurous acid and boil to expel the oxides of nitrogen. To the cold solution add 40 ml. of NH_4OH (sp.gr. 0.96) and 50 ml. of ammonium molybdate solution and shake for 5 minutes. Allow to settle for 10 minutes; for material containing less than 0.02% of phosphorus, allow to stand 30 minutes. Filter and wash 10 times with a 1% solution of KNO_3. Return the precipitate and paper to the precipitating vessel, add 1 to 3 ml. in excess of standard NaOH solution and 25 ml. of water, both free from carbon dioxide, and shake or stir until the precipitate is dissolved. Dilute to 100 ml. with water free from carbon dioxide, add 3 drops of a 0.2% solution of phenolphthalein, and discharge the pink color with standard acid. Finish the titration by adding standard alkali until the reappearance of the pink color. With very low phosphorus material this titration should be corrected by a blank carried through all steps of the method.

Note.—If vanadium is present in amounts over 0.08% it should be reduced by ferrous sulfate and sulfurous acid before precipitation with molybdate.

[7] See p. 1495.

[8] Addition of a little sulfite or sulfurous acid facilitates solution after the baking treatment.

Determination of Sulfur by the Oxidation Method

Proceed as in the Determination of Sulfur by the Gravimetric Method as described in the Tentative Methods of Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron and Wrought Iron (A. S. T. M. Designation: E 30–36 T) of the American Society for Testing Materials.[9]

Notes.—Routine determinations of sulfur can be made by the evolution method provided concentrated hydrochloric acid (sp.gr. 1.19) is used, preferably in all-glass apparatus of the Pulsifer type.

Determination of Silicon by the Nitro-Sulfuric Acid Method

Solutions Required: ***Nitro-Sulfuric Acid.***—Pour 160 ml. of sulfuric acid (sp.gr. 1.84) slowly and with stirring into 660 ml. of water and add 180 ml. of nitric acid (sp.gr. 1.42).

Method.—Dissolve 0.9344 g. of the sample passing a No. 100 sieve [10] with 50 ml. of the nitro-sulfuric acid in a 250-ml. porcelain casserole and evaporate until copious fumes of sulfuric acid are evolved. After the solution has cooled somewhat add 125 ml. of distilled water and 5 ml. of HCl (sp.gr. 1.19). Heat with frequent stirring until all salts are dissolved and immediately filter on a 9-cm. paper. Wash the precipitate with cold dilute HCl (5 : 95) and hot water alternately to complete the removal of soluble salts, and finally with hot water until free from acid. Transfer the filter to a platinum crucible, char the paper carefully, and finally ignite with the crucible covered over a blast lamp or in a muffle furnace at 1050° to 1100° C. for at least 10 minutes; cool in a desiccator and weigh. Add sufficient dilute sulfuric acid (1 : 1) to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights divided by 2 and multiplied by 100 represents the percentage of silicon in the alloy.

Note.—For silico-manganese and manganese-silicon, fuse 0.4672 g. of the former or 0.2336 g. of the latter with 8 g. of sodium peroxide in a pure iron crucible. Dissolve the fusion and evaporate to fumes of sulfuric acid. When acidifying the solution of the fusion with sulfuric acid it is necessary to add some sulfurous acid to dissolve the manganese dioxide which separates out.

FERROCHROMIUM

Determination of Chromium by Fusion with Sodium Peroxide

Solutions Required: ***Potassium Permanganate, 0.1 N.***—Dissolve 3.2 g. of potassium permanganate in 1000 ml. of distilled water, allow to age for at least ten days and filter through purified asbestos. Standardize the permanganate solution against 0.2 g. samples of Bureau of Standards Standard Sodium Oxalate by the procedure given on p. 1431.

Standard Ferrous Ammonium Sulfate.—Dissolve 43 g. of the salt in 250 ml. of cold water, add 40 ml. of sulfuric acid (1 : 3), dilute to one liter with distilled water, and mix thoroughly. Large amounts of the solution can be

[9] See p. 1440.

[10] For detailed specifications for these sieves, see Standard Specifications for Sieves for Testing Purposes (A. S. T. M. Designation: E 11) of the American Society for Testing Materials, 1936 Book of A. S. T. M. Standards, Part II, p. 1413.

conveniently mixed by means of a stream of carbon dioxide from a cylinder. As the ferrous ammonium sulfate solution gradually weakens in reducing power it is necessary to standardize it daily or at the same time the ferrochromium is analyzed. The solution can be standardized against either potassium dichromate or sodium oxalate.

The first method is somewhat simpler and more satisfactory for routine work as the conditions prevailing in both the standardization and in the analysis are practically identical. No " blank " corrections are afterwards necessary where the amounts of dichromate, ferrous salt and permanganate are approximately those prevailing in the analysis. The second method is employed chiefly for checking the accuracy of the results obtained with potassium dichromate and in cases where only occasional analyses are made and pure dichromate is not readily available.

To prepare pure potassium dichromate, recrystallize at least twice the purest grade of the salt obtainable, dry the crystals at 150° C., grind to a fine powder and again dry at 150° C. to constant weight. Keep the prepared salt in a ground-glass stoppered bottle. Transfer 1.0000 g. of the pure dichromate, which contains approximately the same amount of chromium as an 0.5000-g. sample of 70% ferrochromium, to an 800-ml. beaker. Dissolve in cold water, acidify with 40 ml. of sulfuric acid (1 : 3) and dilute with cold water to 500 ml. Add a slight excess of the ferrous sulfate solution, approximately 190 ml., and titrate the excess ferrous salt with 0.1 N permanganate to the first faint permanent darkening of the clear green color.

Example.—The calculations involved are illustrated as follows: In a standardization, 190.0 ml. of the ferrous solution was used and 5.06 ml. of 0.1 N permanganate was required to titrate the excess.

1 ml. of 0.1 N $K_2Cr_2O_7$ contains 0.004903 g. of $K_2Cr_2O_7$
1 g. of $K_2Cr_2O_7$ equals 203.94 ml. of 0.1 N $K_2Cr_2O_7$

then:

203.94 + 5.06 = 209.0 ml. of equivalent 0.1 N solution reduced by the ferrous solution.

$$\frac{209.0}{190} = 1.100, \text{ the 0.1 N normality factor.}$$

In standardizing through sodium oxalate, it is necessary to add the ferrous ammonium sulfate solution by means of an accurately calibrated pipette or burette instead of an automatic pipette. Transfer 100 ml. of the approximately 0.1 N ferrous solution to a 600-ml. beaker, dilute to 300 ml. with cold 5% sulfuric acid, add 2 ml. of phosphoric acid and titrate immediately with 0.1 N $KMnO_4$ to a faint permanent pink color. Determine the " blank " on the same volume of water and acids and deduct. When this method is used it is necessary in the actual analysis to determine a " blank " to counteract the influence of the green color of the chromium sulfate upon the permanganate end point. This " blank " can be determined in the solution used in the analysis and is obtained as described later.

Method.—Transfer 0.5000 g. of the sample of ferrochromium (dried at 105° to 110° C.) to a 30-ml. heavy-walled porcelain crucible. Samples of low-carbon ferrochromium should be crushed to pass through a No. 40 screen, while high-carbon ferrochromium and chromium metal should be reduced to pass a No. 100 screen. Add approximately 8 g. of sodium peroxide and thoroughly

mix the contents of the crucible with a small rod, being careful to clean the rod, which can be done conveniently by scraping with another rod. Cover the mixture with 1 to 2 g. of sodium peroxide. Carefully fuse the contents of the covered crucible, preferably in an electric muffle heated to 600° to 700° C. Fusion for five minutes at a low red heat after the mass has melted will insure complete decomposition. When the charge has melted, the crucible should be given a slight rotary motion to stir up any unattacked particles.

Place the cooled crucible and cover in a 600-ml. beaker and dissolve the contents in 200 ml. of water. When the melt has dissolved, remove the crucible and cover, add 1 g. of sodium peroxide and boil the solution ten minutes to completely decompose the excess of peroxide.

Allow the precipitate to settle and filter through a pad of ignited asbestos, preferably in a Büchner funnel. An asbestos rather than a paper filter should be used, for the alkaline solution extracts reducing matter from paper which would cause low results for chromium. Thoroughly wash the precipitate with hot water, and at no time allow the precipitate to run dry during the filtering and washing. If desired, the precipitate can be subsequently dissolved in dilute sulfuric acid and tested for chromium by adding a slight excess of sodium peroxide; the amount of chromium retained is negligible if the precipitate is filtered and washed as directed.

Cool the filtrate, acidify with 50 ml. of sulfuric acid (1 : 1), again cool to room temperature, transfer to an 800-ml. beaker, dilute with cold water to 500 ml. and add a measured excess of ferrous ammonium sulfate. The point at which reduction is complete can be told by changes in the deep green color which is developed. The ferrous salt can be added either as an approximately 0.12 N solution or in weighed portions from a bottle of the well-mixed salt. If the solution of ferrous salt is used, approximately 180 ml. will be required for a 70% alloy; if the salt is added, 8 g. will usually be sufficient. Titrate the excess of ferrous salt with standard 0.10 N potassium permanganate. The first faint permanent darkening of the clear green color is taken as the end point, which is quite sharp and well defined to the practiced eye. If the ferrous salt has been standardized against dichromate, subtract the required number of milliliters of 0.1 N permanganate from the number of milliliters of 0.1 N ferrous solution (obtained by multiplying the number of milliliters of the approximately 0.1 N ferrous solution by the 0.1 N normality factor). The difference represents the number of milliliters of 0.1 N ferrous solution which multiplied by 0.001733 g. gives the number of grams of chromium present.

Where the ferrous solution has been standardized against sodium oxalate, it is necessary to subtract a " blank " from the permanganate titration. This " blank " is obtained as follows: When the end point is reached and the readings have been noted, add about 5 ml. in excess of the ferrous solution and oxidize the excess of ferrous iron by adding 8 ml. of a 15% solution of ammonium persulfate. *Stir the liquid vigorously for one minute.* Carefully add 0.1 N permanganate to the solution with constant stirring until the same end point is obtained as before. The volume of permanganate required, usually 0.2 to 0.4 ml., constitutes the " blank " to be deducted from the volume of the permanganate titration. For example, in the determination of chromium in an 0.5000-g. sample, 190.0 ml. of a 0.11 N ferrous solution and 11.00 ml. of an 0.1 N permanganate (11.40−0.4 ml. blank) were employed.

The calculations are as follows:

$$190.0 \times 1.100 = 209.0 \text{ ml. of } 0.1 \text{ N ferrous solution}$$
$$209.0 - 11.0 = 198.00 \text{ ml.}$$
$$198.0 \times 0.001734 \times 2 \times 100 = 68.65\% \text{ of chromium}$$

The above calculations are given for exactly 0.1 N permanganate; if the permanganate is not 0.1 N, the volume used must be converted to the equivalent of 0.1 N by multiplying by the proper factor.

Determination of Carbon by the Direct-Combustion Method

Determine carbon by the direct-combustion method described in the Tentative Methods of Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron and Wrought Iron (A. S. T. M. Designation: E 30–36 T) of the American Society for Testing Materials,[11] with the following modifications:

1. Ferrochromium alloys require a furnace temperature of 1150° to 1230° C. in order to yield all of the carbon in the material.

2. The determination is made as given in the reference except that the weighed sample of ferrochromium, 0.5000 g. for 4 to 8% carbon and 3 to 1 g. for 0.10 to 2.00% carbon, is mixed with 1 g. of copper oxide and covered with 2 g. of pure ingot iron drillings in order to facilitate complete combustion.

3. On account of the small weight of sample used, the blanks are important and must be carefully determined.

Determination of Silicon

Low-carbon ferrochromium and chromium metal can be decomposed by means of dilute sulfuric acid, but the high-carbon alloy has to be fused with sodium peroxide. For low-carbon ferrochromium, transfer 0.9344 g. (a double factor weight) to a 250-ml. porcelain casserole, add 60 ml. of sulfuric acid (1 : 4) and warm the covered casserole gently until the reaction is complete. For high-carbon ferrochromium, transfer 0.9344 g. of the sample passing a No. 100 sieve to a 30-ml. pure iron crucible made from No. 20 gage (0.032 in. thickness) ingot iron. Add approximately 8 g. of sodium peroxide, mix thoroughly and fuse as directed under the determination of chromium. When the fusion has solidified, tap the covered crucible, while still warm, on an iron plate to loosen its contents in a solid cake which is then transferred to a 250-ml. casserole. Rinse the crucible with a little water, transfer the solution to the casserole, cover, and carefully add 60 ml. of sulfuric acid (1 : 4) after which the cover glass is rinsed and removed.

Evaporate the solution obtained by either of the above procedures until fumes of sulfuric acid are given off. If chromium sulfate solutions are fumed at too high temperatures or for any great length of time or with too little free acid present, considerable difficulty will occur in dissolving the salts. The fuming should, therefore, be made at a temperature not much higher than that required for evolving the acid. Allow the casserole and contents to partly cool (if permitted to become entirely cold, difficulty may be experienced in getting chromium salts to dissolve), add 100 ml. of warm water while stirring

[11] See p. 1426.

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to prevent the residue from caking on the bottom and boil the solution gently for several minutes to dissolve all salts. Filter, washing the paper several times with cold dilute hydrochloric acid (2%), and then with warm water. Transfer the filter and contents to a platinum crucible, char the paper, carefully ignite to remove carbon, and then heat the covered crucible over a blast lamp or in a muffle furnace at 1050° to 1100° C. for at least 15 minutes. Cool in a desiccator and weigh. Add sufficient dilute sulfuric acid (1 : 1) to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights represents silica which contains 46.72% of silicon.

NOTE.—Crucibles made from pure ingot iron contain only traces of silicon and the amount of silica present in the sodium peroxide used is usually negligible, but "blanks" should be run on new lots of crucibles and of peroxide. All nickel crucibles, even the German "Rein" nickel, contains appreciable amounts of silicon.

FERROVANADIUM

DETERMINATION OF VANADIUM BY THE AMMONIUM PERSULFATE METHOD

Solutions Required: ***Ammonium Persulfate*** ***(15%)***.—Make up as needed by dissolving 15 g. of the salt in 100 ml. of distilled water. This salt should be 95% pure and its purity tested by adding 30 ml. of a standard ferrous sulfate solution to 0.3 g. of the persulfate, then 200 ml. of hot water and titrating the excess ferrous salt with potassium permanganate. One milliliter of 0.1 N ferrous solution equals 0.01141 g. of $(NH_4)_2S_2O_8$.

Potassium Ferricyanide Indicator.—Dissolve 0.1 g. of the salt in 100 ml. of water. This solution should be made up fresh daily.

Standard Ferrous Ammonium Sulfate ***(Approximately 0.1 N)***.—See the Determination of Chromium in Ferrochromium.[12]

Potassium Permanganate ***(0.1 N)***.—See the Determination of Chromium in Ferrochromium.[12] One milliliter of 0.1 N $KMnO_4$ is equivalent to 0.005096 g. of vanadium in the following method.

Method.—Treat 0.5000 g. of the alloy, dried at 105° to 110° C., in a 250-ml. covered beaker with a mixture of 60 ml. of sulfuric acid (1 : 3) and 25 ml. of nitric acid (1 : 1). If the alloy fails to decompose readily because the silicon content is high, it may be necessary to add a small amount of hydrofluoric acid. In this event, a 200-ml. platinum dish should be substituted for the beaker. When the reaction has abated, rinse the cover glass and evaporate the solution until copious fumes of sulfuric acid are evolved. Cool, add 100 ml. of water and heat until the salts are dissolved. Transfer the solution to an 800-ml. beaker, dilute to 400 ml. and to the cooled solution add an approximately 0.1 N solution of potassium permanganate until a strong pink color has developed which remains permanent for thirty seconds. Next reduce the vanadium by the use of an approximately 0.1 N solution of ferrous ammonium sulfate added until a drop of the solution withdrawn from the beaker and placed on a drop of potassium ferricyanide indicator shows ferrous iron present—about 35 ml. of 0.1 N ferrous solution. Add 5 ml. of the ferrous ammonium sulfate in excess, stir the solution at least one minute, oxidize the excess of ferrous sulfate

[12] See p. 1490.

with 8 ml. of 15% ammonium persulfate and stir the solution vigorously for *one minute*. Titrate the solution with 0.1 N potassium permanganate solution, added with constant stirring until a faint pink color appears which remains permanent for 30 seconds. Determine the " blank " by dissolving 0.4 g. of " ingot iron " in 60 ml. of H_2SO_4 (1 : 3) and 5 ml. of nitric acid (sp.gr. 1.42), and putting the solution through all of the operations of the analysis. If the alloy contains an appreciable amount of chromium, a weight of pure $K_2Cr_2O_7$ equivalent to the amount of chromium in the sample is dissolved in the acids with the ingot iron.

Determination of Carbon

See the Determination of Carbon in Ferrochromium by the Direct-Combustion Method.[13] A furnace temperature of 1050° to 1100° C. will suffice for ferrovanadium and complete combustion except in very high-silicon material can be secured without the addition of ingot iron and copper oxide.

Determination of Phosphorus by the Modified Molybdate-Magnesia Method

Solutions Required: ***Ammonium Molybdate.***—

Solution No. 1.—Place in a beaker 100 g. of 85% molybdic acid, mix thoroughly with 240 ml. of distilled water, add 140 ml. of NH_4OH (sp.gr. 0.90), filter, and add 60 ml. of HNO_3 (sp.gr. 1.42).

Solution No. 2.—Mix 400 ml. of HNO_3 (sp.gr. 1.42) and 960 ml. of distilled water.

When the solutions are cold, add Solution No. 1 to Solution No. 2, stirring consantly, then add 0.1 g. of ammonium phosphate dissolved in 10 ml. of distilled water, and let stand at least 24 hours before using.

Magnesia Mixture.—Dissolve 50 g. of $MgCl_2 \cdot 6H_2O$ and 200 g. of NH_4Cl in 1000 ml. of distilled water containing a few milliliters of hydrochloric acid.

Method.—Transfer 4 g. of the sample to a platinum dish of 150 to 200-ml. capacity, add 70 ml. of dilute HNO_3 (5 : 6) and heat the covered dish until vigorous action ceases. Add 1 or 2 ml. of hydrofluoric acid, stir the solution, evaporate to dryness, moisten with 10 ml. of nitric acid (sp.gr. 1.42) and again evaporate to dryness. Moisten the cooled residue with 10 ml. of HNO_3 (sp.gr. 1.42), add 50 ml. of water and wash the contents of the dish into a 400-ml. beaker, rubbing the dish well with a policeman. Remove the last traces of adhering salts with 5 ml. of HCl (sp.gr. 1.19) and hot water. Add 10 ml. of HNO_3 (sp.gr. 1.42) and evaporate to a syrupy consistency. Cool, add 25 ml. of HNO_3 (sp.gr. 1.42) 60 ml. of water, 1 g. of boric acid (to take care of any residual fluoride) and heat gently until solution occurs. Filter through a rapid paper into a 300-ml. Erlenmeyer flask and wash with hot water. Heat the solution to boiling, add about 12 ml. of potassium permanganate solution (1.5%) and continue the boiling until manganese dioxide precipitates. Dissolve the precipitate by the addition of sufficient sulfurous acid added dropwise. About 1 ml. usually suffices. Boil for a few minutes to completely expel oxides of nitrogen. Add to the cold solution 15 ml. of ammonium hydroxide (sp.gr. 0.90) and cool the solution to 15° C.

[13] See p. 1493.

Next reduce the vanadium in the cold (15° C.) solution by ferrous sulfate added in approximately 1.5 g. excess. The use of a 50% solution of the salt furnishes a convenient way of adding the necessary amount. One gram of quinquevalent vanadium requires 5.5 g. of $FeSO_4 \cdot 7H_2O$ for reduction to the quadrivalent state. A 4-g. sample of 30% vanadium alloy, including an excess of 1.5 g., would require 8.1 g. of ferrous sulfate. Too large an excess of ferrous sulfate should be avoided. The addition of ferrous sulfate will change the color of the solution to a deep blue. Add 2 drops of a saturated solution of sulfurous acid, 100 ml. of molybdate reagent, shake for 10 minutes and allow to stand at 15° C. for 4 to 6 hours, or preferably overnight. It is well to let the solution stand in a refrigerator. Filter on a paper of close texture, keeping as much of the precipitate in the flask as possible, and wash the flask and the precipitate with not more than 50 ml. of cold, dilute nitric acid (1 : 99). Set the filtrate and washings aside after thorough mixing and see whether further separation of phosphomolybdate occurs. Dissolve the precipitate on the filter in 20 ml. of dilute ammonium hydroxide (1 : 1) to which have been added 2 g. of citric acid, catch the solution in the original flask containing the bulk of the yellow precipitate and finally wash the filter several times with dilute hydrochloric acid (5 : 95). If the ammoniacal solution of the phosphomolybdate is not clear at this point, heat it to boiling, filter through the same paper, and wash the paper with hot water. In this case, and whenever appreciable amounts as such elements as titanium or zirconium are known to be present in the original material, preserve the paper and ignite it in a small platinum crucible with the paper reserved below.

Render the ammoniacal solution acid with hydrochloric acid, add 20 ml. of magnesia mixture and then ammonium hydroxide (sp.gr. 0.90) slowly until a crystalline precipitate appears, and then finally an excess of 3 to 5% by volume. The volume of the solution at this point should not exceed 100 ml. Allow the solution to stand in a cool place for 4 to 6 hours, or preferably overnight.

Filter, keeping as much of the precipitate as possible in the flask, and wash the flask and the precipitate moderately with dilute ammonium hydroxide (1 : 20). Set the filtrate and washings aside after thorough mixing and see whether further precipitation occurs. Dissolve the precipitate on the filter in 25 ml. of dilute hydrochloric acid (1 : 1), catching the solution in the original flask containing the bulk of the precipitate. Wash the filter thoroughly with dilute hydrochloric acid (5 : 95). In case the original material contains appreciable amounts of the elements mentioned above (titanium or zirconium), add the paper to the one reserved above, ignite, fuse any residue with as little carbonate as possible (not over 0.5 g.), extract the cooled melt with hot water, filter, and add the water solution to the hydrochloric acid solution. Transfer the solution to a 200-ml. beaker. In case the amount of arsenic is known to be very small, add 0.5 to 1 g. of ammonium bromide and boil the hydrochloric acid solution to a volume of 5 to 10 ml. Where large amounts of arsenic were originally present, treat with hydrogen sulfide, digest, filter, and wash with acidulated hydrogen sulfide water. Boil to expel hydrogen sulfide and to reduce the volume to 50 to 75 ml. Add 0.1 to 0.2 g. of citric acid, 2 to 3 ml. of magnesia mixture, make ammoniacal as above, and allow to stand in a cool place for 4 to 24 hours.

Filter, wash with dilute ammonium hydroxide (1 : 20), and ignite the precipitate carefully and at as low a temperature as possible until the carbon has been destroyed and the residue is white. Finally, ignite at approximately 1000° C. to constant weight. Dissolve the ignited residue in 5 ml. of dilute nitric acid (1 : 1) and 20 ml. of water. Filter, wash the residue with hot water, ignite and weigh. Treat with a few drops of hydrofluoric acid, evaporate to dryness, ignite and re-weigh. Subtract any loss of weight from the original weight of the pyrophosphate, and calculate on the basis of this purified magnesium pyrophosphate.

Determination of Sulfur by the Oxidation Method

Transfer 4.57 g. of the sample to a 600-ml. beaker and dissolve it in 75 ml. of HNO_3 (sp.gr. 1.42). The reaction is apt to be very rapid and the acid should be added in small portions to the covered beaker which is preferably kept cooled by immersion in ice water. Effect complete solution by gently warming if necessary.

Add 30 ml. of HCl (sp.gr. 1.19) and evaporate to dryness on the steam-bath. Add 30 ml. more of HCl (sp.gr. 1.19), again evaporate to dryness, and bake for 30 minutes at 105° C. Moisten the residue with 30 ml. of HCl (sp.gr. 1.19) and evaporate on the steam-bath to a volume of 5 ml. Add 5 ml. of HCl (sp.gr. 1.19), dilute to 150 ml. and filter. Wash with warm water.

Adjust the volume of the solution to 250 ml. which should now contain about 3 to 4% by volume of HCl. Warm to 75° C., add 30 ml. of $BaCl_2$ (10%), and allow to stand for 24 to 40 hours.

Filter, with as little transfer of the precipitate as possible, through a paper of close texture. Wash the paper two or three times with cold 1% HCl and seven times with warm water. Ignite the paper and contents in a platinum crucible. Treat the ignited residue with 5 ml. of HCl (sp.gr. 1.19) and transfer the resulting solution to the original beaker containing most of the precipitate of $BaSO_4$. Digest the combined portions of $BaSO_4$ so as to dissolve any barium vanadate. Adjust to 150-ml. volume and 2% acidity, add 8 ml. of 10% $BaCl_2$ solution and allow to stand for 24 hours. Filter on a paper of close texture, wash three times with cold 1% HCl and 10 times with warm water. Ignite the paper in platinum, cool in a desiccator and weigh. A blank should be carried through all steps of the determination. The corrected weight of the ignited barium sulfate multiplied by three is equal to the percentage of sulfur.

Notes.—If desired, the washings can be kept separate and examined for $BaSO_4$ as follows: Evaporate the washings to dryness. Dissolve the slight residue in 50 ml. of hot dilute HCl (2 : 98), add 2 ml. of $BaCl_2$ solution (10%), digest at 70 to 80° C. for two hours, avoiding any undue evaporation. Filter on a small paper of close texture and wash as above. The recovery of $BaSO_4$, which is ordinarily obtained, represents approximately 0.001 to 0.002% of sulfur.

In high-silicon alloys the residue from the initial acid digestion should be evaporated with hydrofluoric and nitric acids, fused with sodium carbonate and the water extract of the melt added to the main solution.

Determination of Silicon by the Nitro-Sulfuric Method

Solutions Required: ***Nitro-Sulfuric Acid.***—Pour 160 ml. of sulfuric acid, (sp.gr. 1.84) slowly and with stirring into 660 ml. of water, and add 180 ml. of nitric acid (sp.gr. 1.42).

Method.—Dissolve 0.9344 g. of the sample passing a No. 100 sieve of low or medium-silicon ferrovanadium in 40 ml. of the nitrosulfuric acid in a 250-ml. porcelain or platinum dish and evaporate the solution until " copious " fumes of sulfuric acid are evolved.

Ferrovanadium containing 4% or more of silicon is not completely soluble in nitric acid and sulfuric acid. In this case, fuse 0.9344 g. of the alloy, thoroughly mixed with 8 g. of sodium peroxide, in a 30-ml. crucible of pure iron. Five minutes heating at a dull red heat after the contents of the crucible have melted will insure complete decomposition of the sample. Allow the fusion to solidify, but before it has entirely cooled tap the covered crucible on an iron plate which will loosen the contents in a solid cake. Transfer the melt to a 250-ml. porcelain casserole, rinse the crucible with warm water and cautiously add the solution to the covered casserole. Next add 150 ml. of sulfuric acid (20% by volume) and evaporate to copious fumes of sulfuric acid. Cool the sulfuric acid solution obtained in either procedure, add 125 ml. of water and heat for a few minutes with frequent stirring until all salts are dissolved. Immediately filter on a 9-cm. paper. Wash the precipitate with cold dilute HCl (5 : 95) and cold water alternately to complete the removal of iron salts, and finally with hot water until free from acid. Transfer the filter to a platinum crucible, char the paper without inflaming and finally ignite the covered crucible in a muffle furnace at 1100° C. for 15–20 minutes. Cool in a desiccator and weigh. Add sufficient dilute H_2SO_4 (1 : 1) to moisten the silica and then a small amount of hydrofluoric acid. Evaporate to dryness, ignite and weigh. The difference in weights divided by 2 and multiplied by 100 represents the percentage of silicon in the alloy.

Determination of Aluminum by the Ether-Hydrochloric Acid Method [14]

Dissolve 2 g. of the sample in 25 to 30 ml. of dilute nitric acid (sp.gr. 1.135) (Note 1). When action ceases, add 5 ml. of hydrochloric acid and evaporate to dryness. Add 10 ml. of hydrochloric acid, evaporate to dryness and bake the residue at a moderate temperature. Dissolve the residue in 10 ml. of hydrochloric acid, add 30 ml. of water, boil and filter. Wash the residue with hot dilute hydrochloric acid (1 : 9) followed by water (Note 2).

Evaporate the solution to dryness on a steam-bath, add 20 ml. of hydrochloric acid and warm gently until complete solution is obtained. Cool the solution in ice water and pass hydrochloric acid gas into it to saturation. Add 20 ml. of ether and continue passing the gas into the cold solution until it is again saturated. Allow the mixture to stand for several hours, keeping it cold by immersing the container in ice water. If the solution becomes warm or if it is not allowed to stand, the separation of hydrated aluminum chloride is not quite complete.

Filter through asbestos (small Büchner-asbestos pad washed once with cold ether-hydrochloric acid mixture immediately before use), wash, by decantation, with a cold mixture of equal parts of strong hydrochloric acid and ether which has been saturated with hydrochloric acid gas. The aluminum chloride retains a little vanadium.

Dissolve the precipitated aluminum chloride in the least possible amount of dilute hydrochloric acid (1 : 9) back into the original beaker, from which all

[14] Gooch-Havens, Am. Journal of Science, **4**, 11–416.

of the precipitate need not have been removed. Evaporate the solution to near dryness on a steam-bath, add 10 ml. of strong hydrochloric acid and pass hydrochloric acid gas into the solution to saturation, add 15 ml. of ether and continue passing hydrochloric acid gas to saturation, keeping the solution cold by means of ice water. Let stand several hours, filter on asbestos and wash with the ether-hydrochloric acid mixture as before.

Dissolve the aluminum chloride in dilute hydrochloric acid (1 : 9) into a 250-ml. beaker, add a few grams of ammonium chloride, make faintly alkaline with ammonia, boil, filter (using paper pulp), wash with hot water, dry, ignite and weigh as Al_2O_3.

According to published data, this method gives a complete separation of aluminum from iron, beryllum, zinc, copper, mercury and bismuth. A little vanadium is carried down in the first separation, but two chloride precipitations seem to give a practically complete separation. The proportion of vanadium retained in the final alumina is hardly appreciable when working on a 35% vanadium alloy.

The effect of chromium is not known; presumably some of it would be included in the Al_2O_3. This could be corrected for by fusing the Al_2O_3 with sodium peroxide and estimating the Cr_2O_3 by color.

Notes.—1. Dilute nitric acid (sp.gr. 1.135) is recommended for solution. While this requires rather long digestion at steam-bath temperature, solution seems to be quite complete even when the alloy is high in silicon. In some cases where silicon is very high it is necessary to use a little hydrofluoric acid with the nitric acid. In this case solution should be effected in a platinum dish, the solution evaporated to dryness and the dry residue transferred to a beaker before treatment with hydrochloric acid. A little dilute hydrochloric acid may be used to loosen any oxides that adhere to the dish.

2. The siliceous residue may retain alumina; it should be ignited in platinum. Silica should be expelled by $HF+H_2SO_4$ and the residue fused with $KHSO_4$. After dissolving the fusion in water plus a little HCl, the liquid is made faintly alkaline with ammonia and boiled. Any iron and alumina precipitate is removed by filtration, washed with water, dissolved in a little hot dilute HCl and added to the solution of the alumina obtained after the first ether-hydrochloric acid separation.

FERROTUNGSTEN AND TUNGSTEN METAL

Determination of Tungsen

Solutions Required: ***Cinchonine Solution.***—Dissolve 125 g. of cinchonine in a mixture of 500 ml. of HCl (sp.gr. 1.19) and 500 ml. of distilled water.

Cinchonine Wash Solution.—Dilute 30 ml. of the above solution to one liter.

Method.—Treat 1 g. of the material passing a No. 100 sieve in a large (60-ml.) platinum crucible with 5 ml. of HF; add HNO_3 drop by drop until the metal dissolves. Add 3 to 4 ml. of H_2SO_4 and evaporate on a steam-bath until HNO_3+HF is expelled. Shake gently over a small Bunsen flame, or heat slowly in a sheet iron "radiator" (described by Hillebrand) [15] until H_2SO_4 fumes strongly. Cool, transfer to a 250-ml. beaker with water, finally wiping the crucible with a little filter paper. A little WO_3 sticks to the crucible; it can not be removed by wiping. Reserve the crucible. Dilute the contents of the beaker to about 150 ml. with water, add 10 ml. of hydrochloric acid (sp.gr. 1.19) and boil for a few minutes. Remove from the source of heat, add 10 ml. of cinchonine solution

[15] U. S. Geological Survey Bulletin No. 700, p. 33.

and digest the solution at 80° to 90° C. with occasional stirring, for 30 to 45 minutes.

Add some paper pulp to the solution, stir the solution and when the tungsten precipitate has settled, filter on a 9-cm. paper containing a little "ashless" filter pulp. Wash thoroughly with hot cinchonine solution and finally several times with warm 1% hydrochloric acid. Gently ignite the filter and residue of crude WO_3 in the crucible in which it was originally treated until the carbon is consumed. Add a few drops of nitric acid and dry in the radiator. Ignite the covered crucible for 5 minutes in the full heat of a Bunsen burner, cool, and weigh. Ignitions may be made at about 750° C. in an electric muffle. As WO_3 is slowly but steadily volatilized at temperatures above 750° C., serious error may result from continued ignition of the tungsten trioxide at the temperature that is specified. Add about 5 g. of Na_2CO_3 and fuse, running the fusion around the side of the crucible to remove all WO_3. Dissolve the fusion in hot water, add alcohol, heat, filter and wash with hot water. Place the filter in the crucible and ignite; add a little Na_2CO_3 and fuse again. Dissolve the fusion in water, filter and wash *very* thoroughly with hot water to remove the last traces of Na_2CO_3; ignite in the same crucible as at first, cool, and weigh. The difference between the weight of crucible plus residue and the weight of crucible plus impure tungstic oxide is $WO_3 \times 0.7931 = W$.

Notes.—At the best, direct determination of tungsten in high-grade metal is subject to inherent errors. Accuracy within 0.2% is all that can be expected by any method.

Determination of Carbon

See the Determination of Carbon in Ferrochromium by the Direct-Combustion Method.[16] The alloy ground to pass a No. 100 sieve and mixed with 2 g. of pure iron is burned in an electric furnace heated at 1050° to 1100° C. A "blank" on the ingot iron must be determined and deducted.

Determination of Phosphorus

Treat 1 g. of the finely powdered sample in a platinum dish, fitted with a gold cover, with 15 ml. of HNO_3 (sp.gr. 1.42), add 3 ml. of HF and warm gently. When action subsides add 3 ml. more of HF. After action subsides, boil, remove cover and if decomposition is not complete add more HF and boil again. When solution is complete, wash off the cover and evaporate at a low heat to a volume of about 10 ml., then add 3 or 4 drops of concentrated permanganate solution and continue evaporation until crusts of WO_3 begin to form at the edges, that is to a volume of about 6 ml. Add 5 ml. of H_2SO_4 and evaporate on the stove at a low heat until HF and HNO_3 are expelled and H_2SO_4 fumes are given off. (Strong heat causes spattering and also causes hard over-baked crusts to form on the bottom of the dish which resist subsequent treatment.) Cool, add 25 ml. of water and boil (by agitating over a Bunsen flame) until all soluble salts are dissolved. Discharge pink color, due to excess permanganate, by adding sulfurous acid drop by drop. The pink color may not be very evident but the SO_2 is added even so to reduce higher oxides of manganese. Boil for a minute or two after adding the SO_2. Add 1.20 g. of pure tartaric acid and,

[16] See p. 1493.

when this is dissolved and the solution is cooled to a temperature of about 50° C., add 20 ml. of NH_4OH (sp.gr. 0.90) diluted with an equal volume of water. The precipitated tungstic acid should dissolve completely, giving a clear solution. The solution becomes hot from the reaction between H_2SO_4 and NH_4OH. While it is still hot, add 10 ml. of magnesia mixture and transfer it from the platinum dish to a 6-oz. glass-stoppered bottle. Set the bottle in ice water and when it is thoroughly cooled add four or five glass beads about 6 mm. in diameter. Stopper it tightly and shake in an efficient shaking machine for at least ten minutes. The agitation should be violent. The beads aid in starting the formation of the magnesium precipitate; after agitation add 15 ml. of strong NH_4OH and return the bottle to the ice-water tank and put into a refrigerator to stand overnight. Phosphorus separates as magnesium ammonium phosphate free from tungsten but containing possibly basic magnesium compounds. After standing overnight filter the solution through a 9-cm. paper containing a little paper pulp and wash the bottle and paper thoroughly by small additions of ammonia wash water (1 part NH_4OH to 3 parts H_2O). Do not attempt to remove all the precipitate from the bottle but remove the beads to the filter. The precipitate consists of magnesium ammonium phosphate and arsenate together with silica and other impurities. Tin, tungsten, molybdenum, vanadium and titanium are eliminated by precipitation with magnesia mixture in the presence of tartaric acid. Dissolve the magnesia precipitate in hot dilute HCl and evaporate to a small volume, say 7 or 8 ml. Add 10 ml. of strong HCl and 0.5 g. of KBr and evaporate to dryness. Take up with 5 ml. of HNO_3 and evaporate to dryness again. The KBr serves to reduce As^v to As'''. The addition of strong HCl and boiling followed by evaporation to dryness eliminates As. Dissolve residue in 60 ml. of HNO_3 (sp.gr. 1.135), filter into a 250-ml. shaking bottle; add 40 ml. of NH_4OH (sp.gr. 0.96), cool to 33° C., add 30 ml. of molybdate solution (Blair) and finish the determination by the alkalimetric method (Handy) described in Blair's Chemical Analysis of Iron.

NOTES.—The usual proportions of HNO_3 and HF are reversed in order to provide a constant excess of HNO_3 to oxidize P. The procedure given takes a little longer than when the sample is treated with HF first and HNO_3 is added a little at a time, but the solution is finally complete. It is necessary to keep the platinum dish covered after action begins, as the reaction is somewhat violent.

The platinum dishes recommended are:

8 cm. in diameter at top;
7.8 cm. in diameter at bottom;
4 cm. high.

They have flat bottoms and are wire-rimmed at the top to give additional stiffness. They weigh 58 to 60 g. each and hold about 175 ml. The covers are made of pure gold (for economy), "dished" like a crucible cover to fit the top of the dishes closely. The dishes have small lips to aid pouring. The "tongue" of the cover overlaps the lip. Ordinary round-bottomed dishes may be used, but the manipulation is much more difficult; there is a greater tendency to spattering and danger of local baking or overheating in evaporating to fumes of H_2SO_4. If the separated WO_3 is overheated locally it does not dissolve readily in NH_4OH. In flat-bottomed dishes, the WO_3 is spread in a thin layer and heat is applied evenly all over the bottom.

A good shaking machine should be used. The magnesia precipitate may be started by shaking the bottles by hand, but it is a tiresome job. The solution must be cold, say 8° or 10° C., when shaking begins.

Permanganate solution is added to insure complete oxidation of phosphorus, as in steel analysis. The color of the permanganate gradually fades in the hydrofluoric nitric solution, but after evaporating to fumes and adding water the solution is usually slightly pink.

The amount of tartaric acid is limited to 1.20 g. since ammonium tartrate retards the formation of the magnesia precipitate. Complete precipitation can only be obtained by brisk agitation and by keeping the solution very cold, followed by long standing in a cold place. By this method determinations started at 3 p.m. may be completed by noon the next day.

Determination of Sulfur and Silicon

Solutions Required: ***Cinchonine Solution.***—Thoroughly wash cinchonine reagent with hot water on a Büchner funnel, dry, and dissolve 125 g. of the washed cinchonine in a mixture of 500 ml. of HCl (sp.gr. 1.19) and 500 ml. of distilled water.

Cinchonine Wash Solution.—Dilute 30 ml. of the above solution to one liter.

Barium Chloride Solution.—One hundred grams of $BaCl_2 \cdot 2H_2O$ to 1000 ml.

Sulfur

Fuse 2 g. of the finely powdered metal, intimately mixed with 8 g. of dry Na_2CO_3 and 2 g. of powdered KNO_3, in a large platinum crucible (40 ml.). The fusion is best done over an alcohol blast flame or in an electric muffle to avoid contamination with sulfur contained in illuminating gas. Leach the fusion with 100 ml. of distilled water in a 250-ml. beaker. Filter into a 12-cm. porcelain casserole and wash the residue several times with hot distilled water. The solution contains practically all of the sulfur and most of the tungsten and silica. The residue contains some of each, but not more than traces of sulfur.

Render the liquid acid with 20 ml. of HCl and evaporate to dryness on a steam-bath, thus precipitating tungstic acid. After the residue is dry, heat it to 110° to 120° C. in an oven to dehydrate silica, take up with 5 ml. of HCl and 50 ml. of water, add 3 ml. of a strong cinchonine solution and boil, or heat just short of the boiling point, for 30 minutes. Let the solution stand for at least three hours and preferably overnight. By means of the cinchonine, all WO_3 is rendered insoluble. Filter through an 11-cm. filter paper (free from ash) which has been liberally treated with an emulsion of filter paper pulp and wash the residue with dilute cinchonine solution. Reserve the residue. The filtrate contains all the sulfur; heat it to boiling and add 10 ml. of barium chloride solution, boil for ten minutes, allow it to stand overnight, filter on a 9-cm. filter paper (free from ash), wash repeatedly but not excessively with hot water, ignite in platinum and weigh as $BaSO_4$. If the work is properly carried out every trace of WO_3 is removed from the solutions and there is no danger of including $BaWO_4$ with the $BaSO_4$. If one suspects that the $BaSO_4$ is not quite pure, it should be fused with a little Na_2CO_3, leached with water and filtered; the filtrate should be acidulated with HCl, a few drops of cinchonine solution added and the solution evaporated to dryness on a steam-bath. The dry residue should be dissolved in a little water, a few drops of HCl added, and any residue filtered off. In the clear filtrate $BaSO_4$ should be again precipitated as before. The weight of $BaSO_4 \times 0.1374 = S$.

" Blanks " on all reagents must be made parallel with the determination; this is important since all sodium carbonate obtainable contains sulfur and

there is sometimes more or less of it in cinchonine. All evaporations should be made over steam and the operations conducted in a place free from sulfur gases.

NOTE.—Evolution of sulfur in a stream of hydrogen saturated with hydrochloric acid as in Johnson's Method is optional.

SILICON

The residue of tungstic oxide from which the solution for the determination of sulfur was filtered contains most of the silica. The residue from leaching the original fusion contains the rest.

Wash the residue from Na_2CO_3 fusion from the filter paper with a fine jet of water into a small casserole, add an excess of HCl and evaporate to dryness on a steam-bath, heat the dry residue at 110° to 120° C. to dehydrate the silica, drench with hydrochloric acid, dilute to 100 ml. with hot water, heat until salts are in solution, and filter on a small filter paper (free from ash). Wash thoroughly with hot dilute HCl (1 : 100) and finally with hot water. Reserve the filter.

Wash the residue of tungstic oxide, silica and filter paper pulp from the filter into a small casserole, add 5 ml. of HCl and heat for a few minutes, then filter again through the same paper and wash it *thoroughly* with hot water. This second washing is necessary to remove sodium salts completely. (The original washing sufficed to remove all of the small amount of sulfur present.) Transfer the well-washed filter and residue to a platinum crucible, add the small filter containing the little silica recovered from the Na_2CO_3 fusion residue and ignite both to constant weight in a platinum crucible. On account of the presence of filter paper pulp, the ignited residue is porous and friable; if paper pulp had not been used the WO_3 would be dense and not easily susceptible to the subsequent treatment. Cool the ignited residue of WO_3 and SiO_2 and weigh it. Add 2 or 3 drops of H_2SO_4 and 5 or 6 ml. of pure HF. Digest at a gentle heat for some time, and then slowly evaporate off the HF. When H_2SO_4 fumes are evolved, cool and again add HF, digest as before, evaporate off the HF, ignite gently to expel H_2SO_4 and heat strongly for ten or fifteen minutes. Cool and weigh. The loss in weight after expulsion is SiO_2 which multiplied by 0.4672 equals silicon.

FERROTUNGSTEN

DETERMINATION OF TUNGSTEN

Proceed as in the Determination of Tungsten in the analysis of Ferrotungsten and Tungsten Metal.[17]

NOTES.—1. Fuming with perchloric acid can be substituted for fuming with sulfuric acid if desired. In this case, add 10 ml. of perchloric acid (60%) after the treatment with HF and HNO_3 and evaporate to strong fumes of perchloric acid. Cool, add 50 ml. of water, transfer the solution to a 400-ml. beaker and proceed as in the case of sulfuric acid.

2. If the alloy contains molybdenum, the weighed tungsten oxide may contain a few hundredths of a per cent of molybdenum as MoO_3. If extreme accuracy is desired, the oxide should be tested colorimetrically. If the molybdenum content of the alloy

[17] See p. 1499.

is unknown, one of the sodium carbonate extracts of the fused impure WO_3 can be treated with tartaric acid, mineral acid and hydrogen sulfide and then, if appreciable molybdenum is indicated, the amount should be determined in the sodium carbonate extract obtained in the duplicate run.

3. At the best, direct determinations of tungsten in high-grade metal is subject to inherent errors. Accuracy within 0.2% is all that can be expected by any method.

Determination of Silicon

Fuse 0.9344 to 1.0416 g. of the sample as described under Determination of Sulfur and Silicon in the Analysis of Ferrotungsten and Tungsten Metal.[18] Leach the fusion with water, acidify with HCl and evaporate to dryness and bake at 110° C. Add 20 ml. HCl (sp.gr. 1.19) and warm until all iron salts appear to have dissolved. Add 200 ml. of boiling water and a little paper pulp. Stir well and filter. Wash the tungstic acid thoroughly with hot dilute HCl (1%). Ignite until carbon is gone, add a drop or two of H_2SO_4, evaporate, and then ignite first at a low temperature and finally at 1000° to 1100° C. for 15 to 30 minutes. Cool the ignited WO_3 and SiO_2 and weigh it. Add 5 or 6 ml. of pure HF and a drop or two of dilute H_2SO_4 (1 : 1), evaporate, and again ignite at 750° C. until constant weight is obtained. The loss in weight, corrected for any SiO_2 in the reagents, multiplied by 100 and divided by the weight of sample taken gives the percentage of silicon.

Determination of Sulfur

Transfer 5 g. of the sample to a 300-ml. platinum dish provided with a platinum cover. Add 100 ml. of HNO_3 (sp.gr. 1.42) and add HF a few drops at a time, while heating, until the alloy has dissolved completely. Rinse and remove the cover. Add 1 g. of $NaNO_3$ and 30 ml. of $HClO_4$ (60%) and evaporate to strong fumes of $HClO_4$. Cool, rinse down with water, and again evaporate to fumes.

Add 100 ml. of water, 10 ml. of cinchonine solution (125 g. of cinchonine, sulfur-free, dissolved in 1 liter of 1 : 1 HCl) and some ashless paper pulp. Stir well, digest for 15 minutes at 60° to 70° C. and filter. Wash the tungstic acid with hot HCl (2%) containing 10 ml. of cinchonine solution to 1 liter. Precipitate the sulfur as described under Determination of Sulfur in Ferromolybdenum.[19]

Determination of Copper, Antimony and Tin

Mix 5 g. of the finely powdered metal with 25 g. of Na_2O_2 in a 50-ml. iron crucible. Fuse carefully over a free flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down quietly. Do not raise the temperature rapidly enough to cause spattering. When the charge is molten, keep the crucible at a low red heat and impart a slight rotary motion to stir up any unattacked particles. At the end of 4 to 6 minutes increase the temperature to bright redness for a minute. Cool the crucible with the cover tightly on and as soon as the melt has solidified, tap the still slightly warm crucible several times on an

[18] See p. 1502.
[19] See p. 1508

iron plate in order to loosen the melt in a solid cake. Transfer the melt to a 600-ml. beaker, cover, treat with 300 ml. of warm water, rinse the crucible and add the rinsings to the beaker. Heat to boiling, cool somewhat, add 20 g. of tartaric acid and then 50 ml. of dilute H_2SO_4 (1 : 1). Heat until a clear solution is obtained. If iron scale remains insoluble, decant the liquid, dissolve the scale in strong acid, using a drop of HNO_3 if necessary, and add the solution to the main solution. If unattacked tungsten metal remains, filter, and make a second fusion on the small residue.

(a) **Separation of Copper from Antimony and Tin.**—Adjust the volume of the solution to a volume of 400 ml., heat to from 65 to 70° C. and pass a rapid stream of H_2S through the solution for 30 minutes. Filter, and wash the precipitated sulfides with dilute H_2SO_4 (5 : 95) containing about 1 g. of tartaric acid per 100 ml. and saturated with H_2S. Return the paper and sulfides to the beaker in which the precipitation was made and treat with 50 ml. of KOH-K_2S solution (prepared by saturating 1 volume of a 10% solution of KOH with H_2S and then adding 3 volumes of the solution). Add 1 g. of Na_2O_2 and heat to boiling in the course of 5 minutes and as the solution is occasionally stirred. Dilute with an equal volume of water, filter into a 400-ml. beaker, and wash with a diluted K_2S solution (1 : 10); reserve the filtrate (*A*).

(b) **Copper.**—Dissolve the residue and determine copper colorimetrically or electrolytically as described under Determination of Copper in Ferromolybdenum.[20]

(c) **Separation of Tin and Antimony.**—Treat the reserved filtrate (*A*) with HCl until the solution is acid and then add 1 ml. per 100 ml. in excess. Filter, and wash with acidulated hydrogen sulfide water. Transfer the paper and sulfides to a 400-ml. beaker, treat with 10 ml. of HCl and add $KClO_3$, a few crystals at a time, as the solution is warmed to from 35° to 40° C. Dilute to 200 ml. and boil gently to expel chlorine. Add 5 g. of oxalic acid, heat to from 60° to 70° C. and pass in a rapid stream of H_2S for 20 to 30 minutes. Filter, and wash thoroughly with hydrogen sulfide water containing 0.5 ml. of sulfuric acid and a few crystals of oxalic acid per 100 ml. Reserve the filter paper and precipitate (*B*) for the determination of antimony.

(d) **Determination of Tin:** ***Standard Solution of Iodine.***—Dissolve 3.97 g. of iodine in a solution of 7 g. of KI in a little water. When solution is complete, dilute to 1 liter and mix thoroughly. One ml. of the solution should represent approximately 0.00185 g. of tin and the exact titer is found by dissolving 0.02 g. of pure tin in HCl, treating with lead as in the method, and titrating. For the small amounts of tin involved, the theoretical titer as based on standardization against pure arsenious oxide can be used.

Apparatus for Reduction of Tin.—The apparatus for reduction is shown in Fig. 186. At the point *A* a small hole about 1 mm. in diameter shall be blown in the glass. The glass rod *B* shall be drawn out at the end and covered with rubber tubing so as to form a light fitting stopper for the end of the tube *C*.

Treat the filtrate with 5 ml. of H_2SO_4 and evaporate to heavy fumes of the acid. Cool somewhat, and dilute with 100 ml. of water. Add 50 ml. of a solution of ferric sulfate (1%) and heat to boiling. Stir vigorously and add dilute NH_4OH (1 : 1) until the solution is alkaline and then add 3 to 5 ml. in excess. Let settle, filter, and wash with hot water. Dissolve the precipitate

[20] See p. 1509.

in 80 ml. of hot dilute HCl (1 : 1) and wash the filter with hot water, collecting the solution (not over 150 ml. in volume) in a 300-ml. Erlenmeyer flask. Add 1 to 2 g. of test lead and close the flask with a one-hole rubber stopper carrying a bent delivery tube, as shown in Fig. 186.

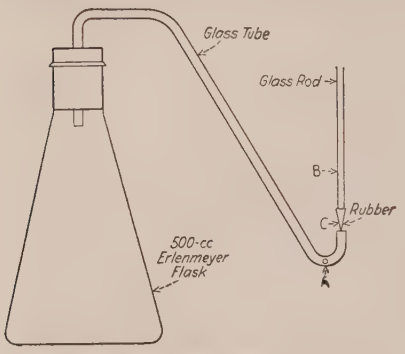


Fig. 186. Apparatus for Reduction of Tin.

Boil gently for 20 minutes. At the end of this period immerse the end of the delivery tube in a small beaker containing about 50 ml. of a strong solution of $NaHCO_3$ and insert the rubber-tipped tube at *C*, Fig. 186. Remove the flask and beaker from the hot plate and cool in a stream of cold water. When cool, remove the stopper, add 5 ml. of freshly prepared starch solution and titrate with the standard solution of iodine to a permanent blue tint. Subtract the volume required in a blank run and multiply by the tin titer of the solution.

(e) **Determination of Antimony.**—Spread the reserved filter paper and precipitate (*B*) side down, on a small watch glass and place this over a beaker containing a few centimeters of HCl and a drop or two of bromine. Warm the beaker until decomposition of the sulfide is complete. Rinse cover and paper with warm dilute HCl (1 : 9), keeping the volume down to 25 ml. Evaporate the solution to about 5 ml. on the steam bath and then add 1 g. of pure ferrous sulfate, 0.5 g. of potassium chloride, and 40 ml. of HCl. Evaporate the solution on the steam bath to a volume of about 5 ml. Dilute with 10 ml. of water, add 1 ml. of HNO_3 and heat until the iron is oxidized. Dilute to 100 ml. heat to boiling, and add dilute NH_4OH until in definite excess. Let settle, filter, and wash with warm water. Dissolve the precipitate in 10 to 15 ml. of hot dilute HCl (1 : 3) containing 0.1 g. of tartaric acid. Dilute to 100 ml., heat and add ammonium bisulfite drop-by-drop to reduce the iron. Boil to expel the excess of SO_2, cool and pass in a rapid stream of H_2S for 15 to 30 minutes. Filter through a weighed Gooch crucible and wash successively with acidulated hydrogen sulfide water, alcohol, ether and carbon disulfide. Heat in a radiator and add a *drop* of HNO_3, from time to time to oxidize the sulfide. Finally heat at about 600° C. and weigh as Sb_2O_4.

FERROMOLYBDENUM

Determination of Carbon by the Direct-Combustion Method

Determine carbon by the direct-combustion method described in the Tentative Methods of Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron and Wrought Iron (A. S. T. M. Designation: E 30–36 T) of the American Society for Testing Materials [21] with the following modifications:

1. It is advisable to use a flux such as ingot iron or red lead, particularly with low-carbon alloys. If fluxes are added, great care shall be taken in obtaining a proper correction for the blank.

[21] See p. 1426.

2. Because of the high sulfur maximum, special provision must be made for the removal of oxides of sulfur in the exit gases. This can be done (*a*) by passing the gases through platinized silica gel heated to 500° C. and then through a column of ironized asbestos; (*b*) by passing through a strong solution of chromic acid or potassium permanganate and then through a desiccant such as magnesium perchlorate; or (*c*) by inserting a 6-in. plug of ironized asbestos in the exit end of the combustion tube and burning out the accumulated sulfate regularly.

Determination of Molybdenum

Solutions and Apparatus Required: ***Ferric Phosphate Solution.***—Dissolve 100 g. of ferric sulfate in 1 liter of water to which 150 ml. of phosphoric acid (sp.gr. 1.73) and 20 ml. of dilute sulfuric acid (1 : 1) have been added.

Standard 0.1 N Potassium Permanganate.—Prepare and standardize the solution as described in the Tentative Methods of Chemical Analysis of Ferro Alloys (A. S. T. M. Designation: A 104–36 T) of the American Society for Testing Materials.[22] One ml. of a 0.1 N solution of $KMnO_4$ represents 0.0067 g. of sodium oxalate, and 0.0032 g. of molybdenum.

Jones Reductor.—The reductor should contain a column of 20 to 30-mesh amalgamated zinc ¾ in. in diameter and 10 in. in length, resting on enough asbestos to prevent particles of zinc from passing into the receiving flask. To amalgamate the zinc, treat it with a solution of $HgCl_2$ (2%) for a few minutes and then wash thoroughly with water. When idle, the reductor should always be kept full to above the top of the zinc with distilled water.

Method

Transfer 0.5 g. of sample to a 150-ml. beaker, cover, treat with 10 ml. of dilute HNO_3 (1 : 3), and warm to complete solution. If solution is difficult, add a drop or two of HF. When reaction is complete, cautiously add 10 ml. of dilute H_2SO_4 (1 : 1), and evaporate to fumes of the acid. Cool, add 40 ml. of water and warm. Rinse and remove the cover. Filter and wash the paper and silica 12 to 15 times with hot water, 3 to 4 times with hot dilute NH_4OH (1 : 3), and finally 4 to 5 times with hot water, the washings being allowed to run into the main filtrate. Discard the silica. Cool, add NH_4OH until it is difficult to avoid a red tint, and heat the still acid solution to boiling. Pour the solution slowly and with vigorous stirring into 75 ml. of nearly boiling dilute NH_4OH (1 : 5) contained in a 500-ml. beaker. Rinse the beaker with a little water, and then with a little hot dilute NH_4OH and add to the main solution. Add a little paper pulp, filter into a 500-ml. beaker, and wash the residue with hot water. Set the filtrate aside. Dissolve the precipitate in a slight excess of hot dilute H_2SO_4 (1 : 4), and nearly neutralize and pour into NH_4OH as before. Filter into the reserved filtrate. Dissolve the precipitate and repeat the operation.

Treat the three combined ammoniacal filtrates with 3 g. of powdered tartaric acid. Stir until dissolved, and saturate the warm solution with H_2S. If a precipitate appears, filter and wash with a dilute solution of $(NH_4)_2S$.

[22] See p. 1490.

Warm the filtrate, cover the beaker, and add dilute H_2SO_4 (1 : 1) until the solution contains 10 ml. in excess for each 100 ml. of solution. Let the solution stand at the side of the steam bath (about 40° C.) for 15 minutes, and let settle. Filter, and wash the sulfide thoroughly with dilute H_2SO_4 (1 : 99) containing 10 g. of tartaric acid per liter and saturated with H_2S.[23]

Transfer the MoS_3 and paper to a 250-ml. beaker, cover, and treat with 6 ml. of H_2SO_4 and 10 ml. of HNO_3. Cautiously heat until fumes of H_2SO_4 are given off. Let cool, add 5 ml. of HNO_3, again heat to fumes, and repeat the treatment until the yellow color due to organic matter has disappeared. Cool, rinse and remove the cover, rinse the inside of the beaker, and add a solution of $KMnO_4$ (2.5%) very *cautiously* until a permanent red tint is obtained. Again evaporate to fumes of H_2SO_4. Cool and add 75 ml. of water. Boil for a few minutes, add 2 g. of pure zinc shot (0.002% of iron or under), and continue the boiling until any copper has been reduced to metal. Filter through a filtering crucible and wash with hot water.

If the Jones reductor has been standing idle, pass 100 ml. of warm (40 to 50° C.) dilute H_2SO_4 (5 : 95) through it, then a little water, and discard the solution. Add 35 ml. of the phosphate solution to the receiver, and then enough water so that the tip of the reductor dips well beneath the solution when the receiver is connected with the reductor. Draw the cool or slightly warm solution of the molybdenum, which should be about 100 ml. in volume and contain about 5 ml. of H_2SO_4, through the reductor as the receiving flask is given slight rotary motion. Just before the surface of the liquid reaches the zinc, add a 50-ml. portion of water, and finally rinse by adding two more portions, each time just before the surface of the solution reaches the zinc. Close the stopcock while a portion of the last washing solution remains in the reductor funnel. Disconnect, and raise the reductor as a little water is allowed to run through the stem, rinse the outside of the stem, and proceed with the titration with the standard 0.1 N solution of $KMnO_4$. Run a blank, subtract the volume of 0.1 N solution required, and multiply the remainder by the molybdenum titer of the solution.

Determination of Sulfur

Transfer 2 to 5 g. of the sample to a 500-ml. casserole and dissolve it in 30 to 75 ml. of HNO_3 (sp.gr. 1.42). The reaction is likely to be very rapid and the acid should be added cautiously to the covered casserole which is preferably kept cooled by immersion in ice water.

Add 30 ml. of HCl (sp.gr. 1.19) and evaporate to dryness on the sand or steam bath. Add 30 ml. more of HCl (sp.gr. 1.19), again evaporate to dryness, and bake for 30 minutes at 105° C. Take up with 25 to 50 ml. of HCl (sp.gr. 1.19) and when solution is complete, dilute with water, and filter to remove silica. Evaporate the filtrate to from 15 to 25 ml. to expel most of the free acid, and dilute to 100 ml. with warm water. Add a little paper pulp, filter, and wash, first with dilute HCl (1 : 99) and then with water. Dilute to 200 ml., add 20 ml. of a solution of $BaCl_2$ (10%), and stir vigorously for several minutes. Allow to stand overnight and filter on a paper of close texture. Wash the paper and $BaSO_4$, 18 to 20 times with cold HCl (1%), 3 or 4 times with NH_4OH (5%) to remove ammonium phosphomolybdate, ignite and weigh. A blank should be run on all reagents used.

[23] Test filtrate for molybdenum by the colorimetric method, p. 1464.

Determination of Phosphorus

Dissolve 2 g. of the finely ground sample in 20 ml. of HNO_3, (sp.gr. 1.42) and 20 ml. of HCl (sp.gr. 1.19). Add 20 ml. of dilute H_2SO_4 (1 : 1) and evaporate to fumes of sulfuric acid. Cool somewhat, add 75 ml. of dilute HCl (1 : 5), heat nearly to boiling and filter. Wash the filter with hot dilute HCl (1 : 5) and dilute the filtrate and washings to 250 ml. Add NH_4OH in slight excess, heat to boiling, boil for 1 to 2 minutes, and let the precipitate settle. Filter through 11-cm. paper of loose texture and wash the precipitate with hot water. Discard the filtrate. Dissolve the precipitate in 25 ml. of hot dilute HCl (1 : 1) and reprecipitate with NH_4OH. Filter, wash a few times with hot water, and discard the filtrate. Dissolve the precipitate in 100 ml. of hot dilute HNO_3 (1 : 3), catching the filtrate in a 300-ml. Erlenmeyer flask. From this point proceed as in the Determination of Phosphorus by the Alkalimetric Method in the analysis of Ferromanganese.[24]

Determination of Copper

Transfer 5 g. of sample to a 400-ml. beaker and dissolve in a slight excess of dilute HNO_3 (1 : 3), adding a few drops of HF if solution is difficult. Cautiously add 25 ml. of H_2SO_4 (sp.gr. 1.84), and evaporate to fumes of sulfuric acid. Cool, treat with 150 ml. of water, filter into a 400-ml. beaker, and wash the residue with water. Nearly neutralize with NaOH and pour into 100 ml. of a warm solution of NaOH (10%). Filter, and discard the filtrate. Dissolve the precipitate in warm, dilute H_2SO_4 (1 : 3) and repeat the precipitation and filtration. Dissolve the precipitate in warm, dilute H_2SO_4 (1 : 3). Cool and treat with 3 g. of powdered tartaric acid. When this has dissolved, add NH_4OH till slightly alkaline, then dilute H_2SO_4 (1 : 1) till just acid, and finally 2 ml. in excess. Add 5 g. of Na_2SO_3, heat nearly to boiling and, slowly and with stirring, add a solution of 1 g. of KCNS in as little water as possible. Add a little paper pulp and digest with occasional stirring for 30 minutes at about 90° C. Filter and wash thoroughly with hot water containing a little tartaric acid and KCNS. Ignite paper and residue in a porcelain crucible at about 700° C. Brush the residue into a 100-ml. electrolysis beaker, add 5 ml. of HNO_3 to the crucible, warm for a few minutes, and pour into the beaker. Heat until the oxide has dissolved and evaporate to 1 to 2 ml. Add 50 ml. of water and determine the copper by electrolysis (see the Determination of Copper in the Tentative Methods of Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron and Wrought Iron (A. S. T. M. Designation: E 30–36 T) of the American Society for Testing Materials [25] if the amount is high, or by the colorimetric method if the amount is small.

[24] See p. 1488.
[25] See p. 1446.

EXAMINATION OF BITUMINOUS SUBSTANCES, INCLUDING ASPHALTS, TARS AND PITCHES [1]

PART I

EXAMINATION OF CRUDE, REFINED AND BLENDED BITUMINOUS SUBSTANCES

The methods ordinarily used for examining bituminous substances and their mixtures may be grouped under four headings, viz.:

(1) Physical characteristics.
(2) Thermal tests.
(3) Solubility tests.
(4) Chemical methods of examination.

TABLE I

Description	For Purposes of Identification	Adaptibility for a Given Purpose	Gauging the Uniformity of Supply	Purposes of Factory Control	As a Criterion of the Quality*
Physical Characteristics:					
Fracture	YES	....	....	....	....
Streak	YES	Yes	....	....	....
Specific gravity	YES	....	Yes	Yes	....
Viscosity	....	YES	Yes	Yes	....
Penetration (Hardness)	YES	YES	YES	YES	....
Ductility	....	YES	Yes	Yes	....
Thermal Tests:					
Fusing or softening-point	YES	YES	YES	YES	....
Volatile matter	Yes	YES	Yes	Yes	....
Evaporation test	Yes	YES	Yes	Yes	....
Flash-point	....	YES	Yes	Yes	....
Fixed carbon	YES	....	....	....	....
Distillation test	Yes	YES	Yes	Yes	YES
Solubility Tests:					
Solubility in carbon disulphide	YES	YES	YES	....	YES
Carbenes	Yes	....	Yes	Yes	YES
Solubility in petroleum naphtha	YES	Yes	Yes	Yes	....
Free carbon in tars	YES	Yes	Yes	....	....
Chemical Tests:					
Water	Yes	....	....	....	YES
Oxygen in non-mineral matter	YES	....	....	....	....
Solid paraffins	YES	....	....	....	....
Sulfonation residue	YES	....	....	....	....
Saponifiable matter	YES	....	Yes	....	YES
Diazo reaction	YES	....	....	....	....
Anthraquinone reaction	YES	....	....	....	....

* (*a*) Purity; (*b*) Care exercised in its preparation; (*c*) Intrinsic value.

[1] By Herbert Abraham.

TABLE II—SYNOPTICAL TABLE OF THE MOST IMPORTANT DISTINGUISHING CHARACTERISTICS OF BITUMINOUS SUBSTANCES

Genus	Species	Member	Specific Gravity at 77° F. (of Non-Mineral Matter)	Engler Viscosity at 212° F. (100 ml.)	Penetration at 77° F.	Fusibility ° F.*	Fixed Carbon, % (Ash-free Basis)	Soluble in Carbon-Disulfide, %	Non-mineral Matter, Insol. in Carbon-disulfide, %	Mineral Ash, %	Carbenes, %	Soluble in Petroleum Naphtha, %	Oxygen in Non-mineral Matter, %	Solid Paraffins, % (Test 33)	Sulfonation Residue, % (in dist. 235–315° C.)	Tar Acids, %	Saponifiable Matter, %	Diazo Reaction	Anthraquinone Reaction
Bitumens	Petroleums	Non-asphaltic	0.75–0.90	.....	Liquid	<32	½–2	98–100	0–½	0–1	0–½	98–100	0–2	10–25	90–100	0	0–2	No	No
		Semi-asphaltic	0.80–0.95	.....	Liquid	<32	2–5	98–100	0–1	0–1	0–1	95–100	0–3	½–10	85–95	0	0–2	No	No
		Asphaltic	0.85–1.00	.....	Liquid	<32	5–10	98–100	0–1	0–1	0–1	90–100	0–5	0–Tr.	80–95	0	0–5	No	No
	Natural Waxes	Ozokerite	0.85–1.00	.....	5–10	140–200	½–10	95–100	0–1	0–5	0–3	75–95	0–2	50–90	90–100	0	0–2	No	No
		Montan wax	0.90–1.00	.....	0–5	170–200	2–10	98–100	0–2	0–2	0–2	80–100	3–6	0–10	0–10	0	50–80	No	No
	Natural Asphalts	<10% mineral matter	0.95–1.12	.....	0–350	60–325	1–25	60–98	0–40	0–10	0–5	25–95	0–2	0–5	90–100	0	0–2	No	No
		>10% mineral matter	0.95–1.15	.....	0–150	60–400	5–25	Tr.–90	0–25	10–90	0–5	Tr.–85	0–2	0–5	90–100	0	0–2	No	No
	Asphaltites	Gilsonite	1.05–1.10	.....	0–3	250–350	10–20	98–100	0–1	Tr.–1	0–½	40–60	0–2	Tr.	85–95	0	Tr.	No	No
		Glance pitch	1.10–1.15	.....	0–5	250–350	20–30	95–100	0–1	Tr.–5	0–1	20–50	0–2	Tr.	85–95	0	Tr.	No	No
		Grahamite	1.15–1.20	.....	0	350–600	30–55	45–100	0–5	Tr.–50	0–80	Tr.–50	0–2	Tr.	80–95	0	Tr.	No	No
Pyrobitumens	Asphaltic Pyrobitumens	Elaterite	0.90–1.05	.....	Rubbery	Inf.	2–5	10–20	70–90	Tr.–10	Tr.–2	5–10	1–5	Tr.	80–90	.....	Tr.–15	No	No
		Wurtzilite	1.05–1.07	.....	0–5	Inf.	5–25	5–10	80–95	Tr.–10	Tr.–2	Tr.–2	0–2	Tr.	90–98	.....	Tr.	No	No
		Albertite	1.07–1.10	.....	0	Inf.	25–50	2–10	85–98	Tr.–10	Tr.–2	Tr.–2	0–3	Tr.	90–98	.....	Tr.	No	No
		Impsonite	1.10–1.25	.....	0	Inf.	50–85	1–6	90–99	Tr.–10	Tr.–2	Tr.–2	0–3	Tr.	90–98	.....	Tr.	No	No
		Asphaltic pyrobituminous shales	1.50–1.75	.....	0	Inf.	2–25	Tr.–3	15–70	30–85	0–Tr.	0–Tr.	0–3	Tr.–3	90–98	.....	Tr.	No	No
	Non-asphaltic Pyrobitumens	Peat (dry)	0.15–1.05	.....	0	Inf.	15–35	2–6	15–98	2–80	0–2	0–5	26–44	.....	.....	.....	Tr.–15	No	No
		Lignite (dry)	1.00–1.25	.....	0	Inf.	25–50	2–15	65–98	2–25	0–1	5–10	15–28	.....	.....	.....	Tr.–5	No	No
		Bituminous coal	1.20–1.40	.....	0	Inf.	35–75	½–2	75–98	2–25	0–½	0–1	3–18	.....	.....	.....	Tr.–1	No	No
		Anthracite coal	1.30–1.60	.....	0	Inf.	60–90	0–½	75–98	2–25	0	0	1–5	.....	.....	.....	0	No	No
		Lignitic and coal shales	1.30–1.75	.....	0	Inf.	20–45	0–1	15–70	30–85	0	0–½	3–15	.....	.....	.....	Tr.–2	No	No
Pyrogenous Distillates	Pyrogenous Waxes	Wax tailings	1.00–1.10	50–100	10–150	60–100	2–8	98–100	0–2	0–Tr.	0–Tr.	95–100	0–2	Tr.–5	95–100	0	Tr.	No	Yes
		Paraffin wax	0.85–0.95	25–50	5–50	100–150	0–2	99–100	0–½	0–½	0	99–100	0–Tr.	95–100	95–100	0	0	No	No
	Petroleum Tars	Carburetted water-gas tar	1.00–1.18	25–50	.....	<0–10	10–20	95–100	0.2–5	0–½	0–2	20–75	1–2	0–5	1–25	0	Tr.–2	Yes	Yes
		Oil-gas tar (Low-temperature)	0.95–1.10	25–50	.....	<0–20	10–25	99–100	0–0.2	0–½	0–2	50–85	1–2	0–5	20–40	0	Tr.	Yes	Yes
		Oil-gas tar (High-temperature)	1.15–1.35	Over 50	.....	30–100	15–35	70–90	10–30	0–½	0–2	25–70	1–2	Trace	Tr.–10	0	Tr.	Yes	Yes
	Coal Tars	Horizontal gas-retort tar	1.18–1.33	150–650	.....	<0–40	15–40	60–85	16–40	0–½	0–2	20–40	1–3	0–Tr.	0–5	1–4	2–5	Yes	Yes
		Inclined gas-retort tar	1.15–1.25	100–300	.....	<0–30	15–40	80–85	15–20	0–½	0–2	20–60	1–3	0–2	5–10	4–6	2–5	Yes	Yes
		Vertical gas-retort tar	1.08–1.16	25–50	.....	<0–25	15–30	94–98	2–5½	0–½	0–2	60–80	1–3	0–5	5–10	5–11	7½–15	Yes	Yes
		Coke-oven coal-tar	1.15–1.26	30–100	.....	<0–25	14–40	83–97	3–17	0–½	0–2	60–75	1–3	0–Tr.	0–5	1–5	2–5	Yes	Yes
		Blast-furnace coal-tar	0.95–1.10	75–100	.....	<0–25	10–25	65–80	10–25	10–15	0–2	50–70	1–3	3–15	15–15	5–15	10–15	Yes	No

TABLE II—SYNOPTICAL TABLE OF THE MOST IMPORTANT DISTINGUISHING CHARACTERISTICS OF BITUMINOUS SUBSTANCES—*Continued*

Genus	Species	Member	Specific Gravity at 77° F. (of Non-Mineral Matter)	Engler Viscosity at 212° F. (100 ml.)	Penetration at 77° F.	Fusibility ° F.*	Fixed Carbon, % (Ash-free Basis)	Soluble in Carbon-Disulfide, %	Non-mineral Matter, Insol. in Carbon-disulfide, %	Mineral Ash, %	Carbenes, %	Soluble in Petroleum Naphtha, %	Oxygen in Non-mineral Matter, %	Solid Paraffins, % (Test 33)	Sulfonation Residue, % (in dist. 235-315° C.)	Tar Acids, %	Saponifiable Matter, %	Diazo Reaction	Anthraquinone Reaction
Pyrogenous Distillates (cont.)	Coal Tars (cont.)	Gas-producer coal-tar	1.12–1.20	100–∞	.....	<0–50	10–30	60–95	5–25	0–25	0–2	50–75	1–3	0–3	0–5	3–9	5–15	Yes	Yes
		Low-temperature coal-tar	0.95–1.12	25–50	.....	<0–25	5–15	90–100	0–7	0–1½	0–1	75–90	1–3	3–15	5–25	10–30	15–40	Yes	No
	Wood Tars	Pine tar	1.05–1.15	±65	.....	0–50	5–15	92–100	0–7½	0–1	0–2	65–95	5–10	0	1–5	10–40	20–60	Yes	No
		Hardwood tar	1.10–1.21	±50	.....	0–20	5–20	95–100	0–5	0–1	0–2	50–90	2–10	0	1–5	5–15	25–85	Yes	No
	Miscellaneous Tars	Peat tar	0.90–1.05	.....	.....	40–60	5–15	97–100	0–3	0–1	0–2	95–100	5–15	5–15	5–15	5–15	5–20	Yes	No
		Lignite tar	0.85–1.05	.....	.....	60–90	5–20	96–100	0–2	0–1	0–2	98–100	5–10	10–25	10–20	5–20	5–25	Yes	No
		Shale tar	0.85–0.95	.....	.....	60–90	5–10	98–100	0–2	0–1	0–2	95–100	1–5	5–15	15–35	0–2	0–5	Yes	No
		Bone tar	0.95–1.05	.....	.....	<0–10	5–15	95–100	0–5	0–½	0–2	95–100	2–8	0	0–5	5–40	5–50	Yes	No
Pyrogenous Residues	Pyrogenous Asphalts	Residual oils	0.85–1.07	.....	100–350	32–110	2–10	98–100	0–½	0–½	0–1	80–99	0–3	0–15	90–100	0	Tr.–5	No	No
		Blown petroleum asphalt	0.90–1.07	.....	25–200	80–400	5–20	95–100	0–5	0–½	0–10	50–90	2–5	0–10	90–100	0	Tr.–2	No	No
		Residual asphalt	1.00–1.17	.....	0–150	80–225	5–40	85–100	0–15	0–1	0–30	25–85	0–2½	0–10	90–100	0	0–2	No	No
		Sludge asphalt	1.05–1.20	.....	0–150	80–225	5–30	95–100	0–5	0–1	0–15	60–95	3–7	0–½	80–95	0	0–2	No	No
		Wurtzilite asphalt	1.04–1.07	.....	5–20	150–300	5–25	98–100	0–¼	Tr.–2	0–2	50–80	0–2	0–Tr.	90–95	0	Tr.	No	No
	Petroleum Pitches	Carburetted water-gas-tar pitch	1.10–1.25	.....	0–100	80–300	25–45	75–98	2–25	0–½	5–10	50–70	0–2	0–5	0–15	0	0–1	Yes	Yes
		Oil-gas-tar pitch	1.15–1.30	.....	0–100	80–300	20–35	70–98	2–30	0–½	5–10	60–80	0–2	0–5	20–40	0	0–1	Yes	Yes
	Coal-tar Pitches	Horizontal gas-retort-tar pitch	1.25–1.40	.....	0–100	80–212	35–65	45–70	30–55	0–½	2–10	10–20	Tr.–2	0	0–3	5–20	Tr.–1	Yes	Yes
		Inclined gas-retort-tar pitch	1.25–1.35	.....	0–100	80–212	30–45	63–78	28–37	0–½	2–10	15–30	Tr.–2	0	2–6	10–15	Tr.–1	Yes	Yes
		Vertical gas-retort-tar pitch	1.15–1.30	.....	0–100	80–300	15–40	70–94	6–30	0–½	2–10	20–40	Tr.–2	0–Tr.	4–7	20–30	Tr.–1	Yes	Yes
		Coke-oven-coal-tar pitch	1.20–1.35	.....	0–100	80–300	17–60	50–92	8–50	0–½	2–10	10–30	Tr.–2	0	0–5	1–12	Tr.–1	Yes	Yes
		Blast-furnace coal-tar pitch	1.20–1.30	.....	0–100	80–212	10–30	45–75	15–35	10–20	1–5	5–25	Tr.–2	2–5	15–25	20–30	Tr.–1	Yes	No
		Gas-producer-tar pitch	1.20–1.35	.....	0–100	80–212	25–45	60–85	15–40	0–2	2–10	10–30	Tr.–2	0–Tr.	0–5	10–15	Tr.–1	Yes	Yes
		Low-temperature-tar pitch	1.10–1.26	.....	0–100	80–200	8–22	85–98	2–15	0–3	1–5	25–60	Tr.–2	2–5	5–20	25–50	Tr.–1	Yes	No
	Wood-tar Pitches	Pine-tar pitch	1.10–1.20	.....	0–100	100–212	10–25	40–90	2–60	0–1	0–5	25–80	2–8	0	1–4	10–25	45–75	Yes	No
		Hardwood-tar pitch	1.20–1.30	.....	0–100	100–212	15–35	30–95	5–70	0–1	2–10	15–50	1–5	0	Tr.–5	30–60	60–95	Yes	No
	Miscellaneous Pitches	Rosin pitch	1.08–1.15	.....	10–100	120–200	10–20	98–100	0–2	0–1	0–5	90–100	5–10	0	Tr.–5	.....	25–95	Yes	No
		Peat-tar pitch	1.05–1.15	.....	0–100	100–250	10–30	95–100	0–5	0–1	0–5	65–95	2–8	2–5	5–10	25–40	0–5	Yes	No
		Lignite-tar pitch	1.05–1.20	.....	0–100	80–250	10–40	95–99	0–2	0–1	0–5	60–85	2–5	1–5	10–25	30–50	0–8	Yes	No
		Bone-tar pitch	1.10–1.20	.....	0–100	80–225	15–25	85–99	1–15	0–½	0–10	75–95	0–2	0	0–5	.....	2–25	Yes	No
		Fatty-acid pitch	0.90–1.10	.....	5–>350	35–225	5–35	95–100	0–5	0–5	0–5	80–100	2–10	Tr.	0–5	.....	5–98	No	No

* R. and B. Method for bitumens, asphaltic pyrobitumens, pyrogenous wax and pyrogenous asphalts; Cube Method for tars and pitches.

In general, these tests may have one or more of the following objects in view:
(*a*) To serve as a means of identification.
(*b*) To ascertain the value of the substance for a given purpose.
(*c*) To gauge its uniformity of supply.
(*d*) As an aid to factory control in its preparation, refining or blending.
(*e*) As a criterion of its quality.

The most important methods of testing are given in Table I.

Table II gives a list of the principal bituminous substances, together with such of their physical and chemical characteristics as will enable them to be distinguished, one from another.

PHYSICAL CHARACTERISTICS

Fracture

This is ascertained upon cleaving the specimen by subjecting it to a sharp blow, and examining the cleavage surface. Only hard and "brittle" bituminous substances will yield to this test, including the hard asphalts and asphaltites. The fracture may either appear conchoidal (rounded and curved like a shell), or hackly (jagged, irregularly and rough).

Streak

This represents the color of the powder which is left behind on drawing a piece of the solid bituminous material across the surface of unglazed porcelain. Hard bituminous materials only will yield to this test. The streak may be classified as white (where no streak is visible), yellowish, yellowish brown, brown, brownish black and black.

Specific Gravity

Hydrometer Method.—Where speed is essential and great accuracy not required, the specific gravity of fluid bituminous materials may be determined with a hydrometer having its scale sub-divided to unity in the third place of decimals. Usually a series of hydrometers are used, ranging respectively from 0.800 to 0.900, 0.900 to 1.000, 1.000 to 1.080, 1.070 to 1.150, 1.150 to 1.230, and in such dimensions as to enable them to be used in a 100 ml. cylinder approximately 300 mm. long having an inside diameter of not less than 32 mm. as illustrated in Fig. 187. The hydrometer shall conform to the following requirements as to dimensions:

	Dimension	Permissible Variation
Length of stem	125 mm.	6 mm.
Length of bulb	105 mm.	5 mm.
Length of scale	80 mm.	4 mm.
Diameter of stem	6 mm.	0.5 mm.
Diameter of bulb	22 mm.	1 mm.

Most hydrometers are adapted to read at 60° F./60° F., or in other words, the instruments are calibrated for water at 60° F. taken as unity. The standard temperature for testing bituminous materials is 77° F., and they should accordingly be brought to this temperature when tested with the hydrometer. For correcting the reading to water at 77° F., it should be multiplied by 1.002, as follows:

$$\text{Sp.gr. at } 77° \text{ F./}77° \text{ F.} = \text{Sp.gr. at } 77° \text{ F./}60° \text{ F.} \times 1.002.$$

In running the test, the bituminous material is brought to 77° F., immediately poured into the hydrometer jar, and then the hydrometer allowed to

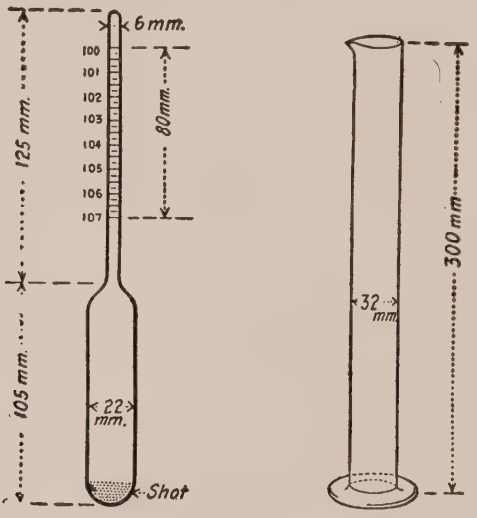


Fig. 187.—Hydrometer for Liquid Bituminous Substances.

sink into it until it comes to a definite resting-point, whereupon it is raised slightly, and allowed to sink a second time. The reading is then noted. The hydrometer must not be pushed below the point at which it comes to rest until after the second reading has been taken, whereupon it should be pushed a slight distance below the end-point to observe whether or not it will rise. If it fails to do so, it is evident that the bituminous material is too viscous to be tested by the hydrometer method, and some other method should be employed. Care should be taken that the hydrometer does not touch the sides or bottom of the cylinder when the reading is taken, also that the surface of the liquid is free from froth or bubbles.

The hydrometer has also been recommended for ascertaining the specific gravity of hard asphalts, which are melted and tested while fluid at elevated temperatures, the results being converted to 60°/60° F. by suitable conversion tables.

For converting specific gravity into degrees Baumé and vice versa, the following formulae may be used:

For liquids lighter than water:

$$°\text{Baumé} = \frac{140}{\text{Sp.gr. } 60°/60° \text{ F.}} - 130$$

$$\text{Sp.gr. } 60°/60° \text{ F.} = \frac{140}{130 + °\text{Baumé}}$$

For liquids heavier than water:

$$°\text{Baumé} = 145 - \frac{145}{\text{Sp.gr. } 60°/60° \text{ F.}}$$

$$\text{Sp.gr. } 60°/60° \text{ F.} = \frac{145}{145 - °\text{Baumé}}$$

Pyknometer Method.—This method has been standardized as follows:

(*A*) The specific gravity of road oils, road tars, asphalt cements and soft tar pitches shall be expressed as the ratio of the weight of a given volume of the material at 25° C. (77° F.) to that of an equal volume of water at the same temperature and shall be expressed thus:

Specific Gravity 25° C. (77° F.)/25° C. (77° F.)

The determination of specific gravity shall be made with a pyknometer or weighing bottle (Fig. 188), which shall consist of a straight-walled glass tube approximately 70 mm. long and 22 mm. in diameter, carefully ground to receive an accurately fitting solid glass stopper with a hole of 1.5 to 1.7-mm. bore in place of the usual capillary opening. The lower part of the stopper is made concave in order to allow all air bubbles to escape through the bore. The depth of the cup-shaped depression shall be about 4.8 mm. at the center. The stoppered tube should have a capacity of about 24 ml. and when empty should weigh not over 35 g.

Fig. 188.—Pyknometer or Weighing Bottle.

Before making a determination, the pyknometer with stopper shall first be calibrated by weighing it clean and dry upon an analytical balance. This weight is called *a*. It shall then be filled with freshly boiled distilled water at a temperature of 25° C. (77° F.), the stopper firmly inserted, all surplus moisture wiped from the surface with a clean dry cloth and again weighed. This weight is called *b*.

When determining the specific gravity of road oils or road tars which flow readily, the material shall be brought to a temperature of 25° C. (77° F.) and poured into the pyknometer until it is full, with care to prevent the inclusion of air bubbles. The stopper is then firmly inserted and all excess of material forced through the opening is carefully removed with a clean dry cloth. The pyknometer and contents are then weighed and this weight is called *c*. The specific gravity of the material shall be calculated from the formula:

$$\text{Specific Gravity} = \frac{c - a}{b - a}$$

When determining the specific gravity of tar and asphalt products which are too viscous for the method described in the preceding paragraph, a small amount of the material shall be brought to a fluid condition by the gentle application of heat, care being exercised to prevent loss by evaporation. When sufficiently fluid, enough is poured into the clean dry pykometer to about half fill it. Precautions shall be taken to keep the material from touching the sides of the tube above the final level and to prevent the inclusion of air bubbles. The tube should be slightly warmed before filling. The pyknometer and contents are then cooled to room temperature and weighed with the stopper. This weight is called *c*. The pyknometer is next removed from the balance, filled with freshly boiled distilled water, and the stopper firmly inserted. It is then completely immersed for not less than thirty minutes in a beaker of distilled water maintained at 25° C. (77° F.) after which it is removed, and all surplus water is wiped off with a clean cloth. It is immediately weighed. This weight is called *d*. The specific gravity of the material shall be calculated from the formula:

$$\text{Specific Gravity} = \frac{c-a}{(b-a)-(d-c)}$$

When making the specific gravity determination it is important that:

(*a*) Only freshly boiled distilled water shall be used.

(*b*) When weighing the pyknometer completely filled, the temperature of its contents shall be within 1° C. (1.8° F.) of 25° C. (77° F.).

(*c*) Precautions shall be taken to prevent expansion and overflow of the contents from the heat of the hand when wiping the surface of the pyknometer.

(*d*) The presence of all air bubbles shall be eliminated in filling the pyknometer and inserting the stopper.

(*e*) Weighings shall be made quickly after filling the pyknometer and shall be accurate to 1 mg. A number of trial fillings and catch weights may be necessary to obtain the desired degree of accuracy.

(*f*) To prevent breakage of the pyknometer when cleaning it out after a determination has been made upon a very viscous or semi-solid material, it will be found advisable to warm it in an oven at not over 100° C. until most of the material may be poured out and then to swab it with a piece of soft cloth or cotton waste. When cool it may be finally rinsed with carbon disulfide, benzol or other solvent and wiped clean.

The limit of accuracy of the test is ±0.005 specific gravity.

(*B*) The specific gravity of creosote oil fractions is determined in a similar manner by means of a pyknometer, but in this case the results are expressed at 38° C. (100° F.)/15.5° C. (60° F.).

(*C*) The pyknometer method may also be used for finding the specific gravity of hard and brittle bituminous substances, including hard asphalts of high fusing-point, asphaltites, asphaltic pyrobitumens, non-asphaltic pyrobitumens and pyrobituminous shales. Approximately 3.5 grams of the material ground to 60-mesh are carefully weighed and introduced into a 50-ml. pyknometer, with about 30 ml. of distilled water. A vertical condensing bulb is attached to the pyknometer with a small section of rubber tubing, the open end being connected with an aspirator to maintain a partial vacuum. The pyknometer is then boiled on a water-bath to expel all the air from the sample. The

inside of the condensing tube is then washed back into the pyknometer, which is cooled to the desired temperature, stoppered, filled to the mark with water at the same temperature and weighed. The specific gravity may then be calculated from the foregoing formula.

Analytical Balance Method.—This method is adapted for substances which can be melted and cast in a mold to form a briquette which may be handled on cooling. It has been standardized as follows:

The determination of specific gravity shall be made with an analytical balance equipped with a pan-straddle or other stationary support (Fig. 189).

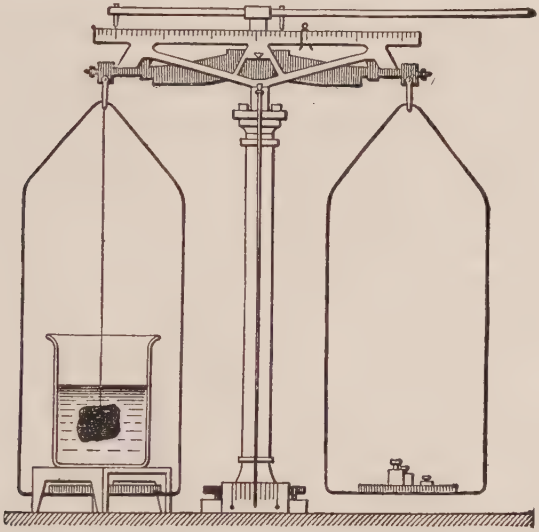


FIG. 189.—Analytical Balance for Ascertaining the Specific Gravity.

The test specimen shall be a cube of the material measuring approximately ½ in. to the edge. It shall be prepared by melting a small sample of the material by the gentle application of heat, care being exercised to prevent loss by evaporation, and pouring when sufficiently fluid into a ½-in. brass cubical mold, having the form illustrated in Fig. 194, which has been amalgamated with mercury and which is placed on an amalgamated brass plate. Precautions should be taken to prevent the inclusion of air bubbles. The hot material should slightly more than fill the mold and when cool the excess may be cut off with a hot spatula. The specimen shall be removed from the mold when cooled to room temperature.

The balance shall first be tared with a piece of fine waxed silk thread sufficiently long to reach from the hook on one of the pan supports to the straddle or rest. The test specimen shall then be attached to the thread, so as to be suspended about 1 in. above the straddle from the hook on the pan support, and weighed. This weight is called *a* and shall be accurate to 0.1 mg. The specimen, still suspended by the thread, shall then be weighed completely immersed in freshly boiled distilled water at 25° C. (77° F.)±1° C. (1.8° F.),

adhering air bubbles being first removed with a fine wire. This weight is called b and shall be accurate to 0.1 mg. The specific gravity of the material shall be calculated from the formula:

$$\text{Specific Gravity} = \frac{a}{a-b}$$

The limit of accuracy of the test is ± 0.005 specific gravity.

Viscosity

Engler Method.—This method as described on p. 1718 is adapted for examining liquid or semi-liquid bituminous substances.

Saybolt Method.—The details of this method will be found on p. 1719.

Float Test.—This instrument is used largely for testing the viscosity or consistency of semi-solid bituminous materials. The range of the float test is limited, and it cannot be used with very fluid bituminous materials or with hard solids. It accordingly fills the gap between the Engler viscosimeter on one hand, and the needle penetrometer on the other. The test is not affected by the presence of finely divided mineral matter or free carbon.

The procedure has been standardized as follows:

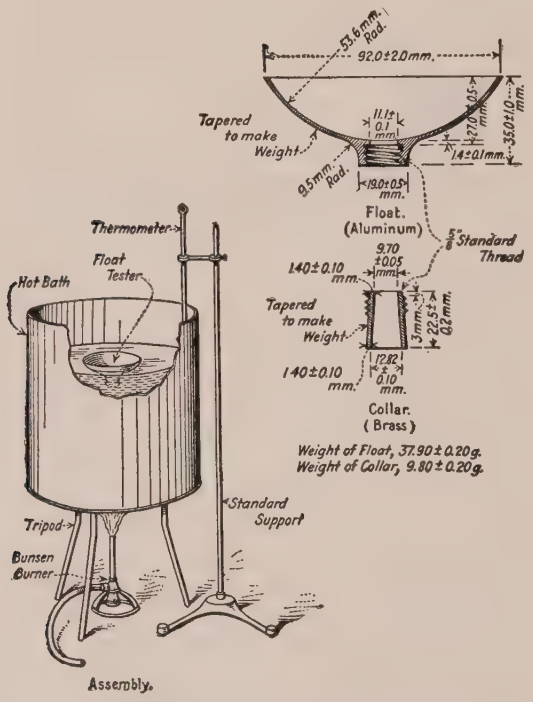


Fig. 190.—Float Test Apparatus.

The float (Fig. 190) shall be made of aluminium or aluminium alloy and shall be in accordance with the following requirements:

	Minimum	Normal	Maximum
Weight of float, g	37.70	37.90	38.10
Total height of float, mm	34.0	35.0	36.0
Height of rim above lower side of shoulder, mm	26.5	27.0	27.5
Thickness of shoulder, mm	1.3	1.4	1.5
Diameter of opening, mm	11.0	11.1	11.2

The collar shall be made of brass and shall be in accordance with the following requirements:

	Minimum	Normal	Maximum
Weight of collar, g	9.60	9.80	10.00
Over-all height of collar, mm	22.3	22.5	22.7
Inside diameter at bottom, mm	12.72	12.82	12.92
Inside diameter at top, mm	9.65	9.70	9.75

The top of the collar shall screw up tightly against the lower side of the shoulder.

The assembled float and collar, with the collar filled flush with the bottom and weighted to a total weight of 53.2 g., shall float upon water with the rim 8.5 $\pm$1.5 mm. above the surface of the water. Dimensions of the apparatus additional to those required above are given in Fig. 190. The thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being $-2°$ to $+80°$ C. or $+30°$ to $+180°$ F., respectively. The diameter of the bath and the depth of water shall be at least 185 mm.

The brass collar shall be placed with the smaller end on a brass plate which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chloride or nitrate, and then with mercury.

The sample shall be completely melted at the lowest possible temperature that will bring it to a sufficiently fluid condition for pouring, excepting creosote oil residues, which shall be mixed and poured at a temperature of 100° to 125° C. It shall be stirred thoroughly until it is homogeneous and free from air bubbles. The sample shall then be poured into the collar in any convenient manner until slightly more than level with the top.

Asphalt and Asphalt Products.—Asphalt and asphalt products shall be cooled to room temperature, placed in water maintained at 5° C. for five minutes, after which the surplus material shall be removed by means of a spatula, or steel knife, which has been slightly heated. The collar and plate shall then be placed in a tin cup containing ice water maintained at 5° C., $\pm$1° C., and left in this bath for at least fifteen minutes.

Tar Products.—Tar products shall be immediately immersed in ice water maintained at 5° C. for five minutes, after which the surplus material shall be removed by means of a spatula or steel knife, which has been slightly heated.

The collar and plate shall then be placed in a tin cup containing ice water maintained at 5° C., ±1° C., and left in this bath for at least fifteen minutes.

The bath shall be filled with water and the water heated to the temperature at which the test is to be made. This temperature shall be accurately maintained and shall at no time throughout the test be allowed to vary more than 0.5° C. from the temperature specified.

After the material to be tested has been kept in the ice water for not less than fifteen minutes nor more than thirty minutes, the collar with its contents shall be removed from the plate and screwed into the aluminium float and immersed in water at 5° C. for one minute. Any water shall then be removed from the inside of the float and the latter immediately floated in the warm bath. As the plug of material becomes warm and fluid, it is forced upward and out of the collar until the water gains entrance into the saucer and causes it to sink.

The time in seconds between placing the apparatus on the water and when the water breaks through the material shall be determined by means of a stop watch, and shall be taken as a measure of the consistency of the material under examination.

NOTE.—Special precautions should be taken to insure the collar fitting tightly into the float and to see that there is no seepage of water between the collar and float during the test.

Penetration (Hardness)

Penetration is defined as the consistency of a bituminous material, expressed as the distance that a standard needle vertically penetrates a sample of the material under known conditions of loading, time and temperature. Where the conditions of test are not specifically mentioned, the load, time and temperature are understood to be 100 g., 5 seconds, 25° C. (77° F.), respectively, and the units of penetration to indicate hundredths of a centimeter.

The container for holding the material to be tested shall be a flat-bottom, cylindrical metal or glass dish, 55 mm. ($2\frac{3}{16}$ in.) in diameter and 35 mm. ($1\frac{3}{8}$ in.) deep. The needle (Fig. 191) for this test shall be made from a cylindrical

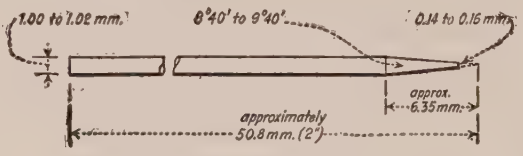


FIG. 191.—Needle for Penetration Test.

steel rod approximately 50.8 mm. (2 in.) long, and having a diameter of 1.00 to 1.02 mm. This shall be symmetrically tapered at one end to a cone approximately 6.35 mm. ($\frac{1}{4}$ in.) in height and whose angle shall be within the range if 8° 40′ and 9° 40′. After tapering, the point shall be "blunted" by grinding off to a truncated cone, the smaller base of which shall be from 0.14 to 0.16 mm. in diameter. The finished needle shall be hardened and highly polished.

The water bath shall be maintained at a temperature not varying more than 0.1° C. from 25° C. (77° F.). The volume of water shall be not less than 10 liters and the sample shall be immersed to a depth of not less than 10 cm.

(4 in.) and shall be supported on a perforated shelf not less than 5 cm. (2 in.) from the bottom of the bath. Any apparatus which will allow the needle to penetrate without appreciable friction, and which is accurately calibrated to yield results in accordance with the definition of penetration, will be acceptable.

The transfer dish for container shall be a small dish or tray of such capacity as will insure complete immersion of the container during the test. It shall be provided with some means which will insure a firm bearing and prevent rocking of the container.

The sample shall be completely melted at the lowest possible temperature and stirred thoroughly until it is homogeneous and free from air bubbles. It shall then be poured into the sample container to a depth of not less than 15 mm. ($\frac{5}{8}$ in.). The sample shall be protected from dust and allowed to cool in an atmosphere not lower than 18° C. (65° F.) for one hour. It shall then be placed in the water bath along with the transfer dish and allowed to remain one hour.

In making the test, the sample shall be placed in the transfer dish filled with water from the water bath of sufficient depth to completely cover the container. The transfer dish containing the sample shall then be placed upon the stand of the penetration machine. The needle loaded with specified weight shall be adjusted to make contact with the surface of the sample. This may be accomplished by making contact of the actual needle-point with its image reflected by the surface of the sample from a properly placed source of light. Either the reading of the dial shall then be noted or the needle brought to zero. The needle is then released for the specified period of time, after which the penetration machine is adjusted to measure the distance penetrated.

At least three tests shall be made at points on the surface of the sample not less than 1 cm. ($\frac{3}{8}$ in.) from the side of the container and not less than 1 cm. ($\frac{3}{8}$ in.) apart. After each test the sample and transfer dish shall be returned to the water bath and the needle shall be carefully wiped toward its point with a clean, dry cloth to remove all adhering bitumen. The reported penetration shall be the average of at least three tests whose values shall not differ more than four points between maximum and minimum.

When desirable to vary the temperature, time and weight, and, in order to provide for a uniform method of reporting results when variations are made, the samples shall be melted and cooled in air as above directed. They shall then be immersed in water or brine, as the case may require, for one hour at the temperature desired. The following combinations are suggested:

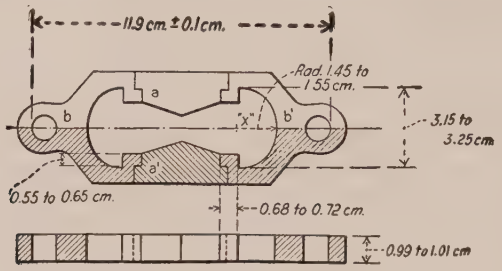
At 0° C. (32° F.) 200-g. weight, 60 seconds.
At 46.1° C. (115° F.) 50-g. weight, 5 seconds.

Ductility

This test has been standardized as follows:

The ductility of a bituminous material is measured by the distance to which it will elongate before breaking when two ends of a briquet of the material of the form described, are pulled apart at a specified speed and at a specified temperature. Unless otherwise specified, the test shall be made at a temperature of 25° C. ±0.5° C. (77° F. ±0.9° F.) and with a speed of 5 cm. per minute (±5.0%).

The mold shall be similar in design to that shown in Fig. 192. Dimensions shall be as given with the permissible variations indicated. The mold shall be made of brass, the ends, b and b', being known as clips, and the parts, a and



The opening in the end of each clip, as indicated by "x," shall be half an ellipse having a transverse axis of 3.2 cm. ±0.05 cm. and half of the longitudinal axis shall be 1.45 to 1.55 cm.

Fig. 192.—Mold for Ductility Test Specimens.

a', as sides of the mold. The dimensions of the mold shall be such that, when properly assembled, it will form a briquet having the following dimensions:

Total length	7.45 to 7.55 cm.
Distance between clips	2.97 to 3.03 cm.
Width at mouth of clip	1.98 to 2.02 cm.
Width at minimum cross-section (halfway between clips)	0.99 to 1.01 cm.
Thickness throughout	0.99 to 1.01 cm.

The water bath shall be maintained at the specified test temperature varying not more than 0.1° C. (0.18° F.) from this temperature. The volume of water shall be not less than 10 liters and the sample shall be immersed to a depth of not less than 10 cm. and shall be supported on a perforated shelf not less than 5 cm. from the bottom of the bath.

For pulling the briquet of bituminous material apart, any apparatus may be used that is so constructed that the briquet will be continuously immersed in water as specified, while the two clips are pulled apart at a uniform speed, as specified, without undue vibration.

The bituminous material to be tested shall be completely melted until thoroughly fluid by heating it in an oil bath maintained at the minimum temperature needed to properly liquefy the sample. It shall then be strained through a No. 50 sieve and, after a thorough stirring, poured into the mold. The mold shall be assembled on a brass plate and, so as to prevent the material under test from sticking, the surface of the plate and interior surfaces of the sides aa', of the mold shall be thoroughly amalgamated.[2] The plate upon which the mold is placed shall be perfectly flat and level so that the bottom surface of the mold will touch it throughout. In filling the mold, care shall be taken not to disarrange the parts and thus distort the briquet. In filling, the

[2] The amalgamation may best be effected by immersing the clean mold in a solution of mercury bisulphate containing free metallic mercury, and so as to come in contact with the latter. Instead of mercury, the metal mold, preferably of stainless steel, may be moistened with glycerol.

material shall be poured in a thin stream back and forth from end to end of the mold until it is more than level fiull. It shall be left to cool to room temperature and then placed in the water bath maintained at the specified temperature of test for 30 minutes, after which the excess bitumen shall be cut off by means of a hot straight-edged putty knife or spatula so that the mold shall be just level full.

NOTE.—When paving asphalt cements are being tested, the oil bath shall be maintained at a temperature of from 125 to 150° C. (257 to 302° F.).

The brass plate and mold, with briquet, shall then be placed in the water bath and kept at the specified temperature for at least 1½ hours, when the briquet shall be removed from the plate, the side pieces detached, and the briquet immediately tested. The rings at each end of the clips shall be attached to the pins or hooks in the ductility machine and the two clips pulled apart at a uniform speed as specified until the briquet ruptures. A variation of ±5% from the speed specified will be allowed. The distance through which the clips have been pulled to produce rupture shall then be measured in centimeters. While the test is being made, the water in the tank of the ductility machine shall cover the sample both above and below it by at least 2.5 cm. and shall be kept continuously at the temperature specified within ±0.5° C. (±0.9° F.).

A normal test is one in which the material between the two clips pulls out to a point or thread until rupture occurs at the point where the thread has practically no cross-sectional area. The average of three normal tests shall be taken and reported as the ductility of the sample.

If the bituminous material comes in contact with the surface of the water or the bottom of the bath, the test shall not be considered normal.

NOTE.—When the specific gravity of the bituminous material to be tested is below 0.98 or above 1.01, the specific gravity of the water bath in the ductility machine shall be made the same as the material to be tested by the addition of either methyl alcohol or sodium chloride.

If a normal test is not obtainable on three successive tests, the ductility shall be reported as being unobtainable under the conditions of the test.

THERMAL TESTS

Fusing or Softening-Point

Ring-and-Ball Method.—This has been standardized as follows:

The softening of bituminous materials generally takes place at no definite moment or temperature. As the temperature rises, they gradually and imperceptibly change from a brittle or exceedingly thick and slow-flowing material to a softer and less viscous liquid. For this reason the determination of the

softening-point must be made by a fixed, arbitrary and closely defined method if the results obtained are to be comparable.

The apparatus shall consist of the following:

(*a*) A brass ring 15.875 mm. (5/8 in.) in inside diameter and 6.35 mm. (1/4 in.) deep; thickness of wall, 2.38 mm. (3/32 in.); permissible variation on inside diameter and thickness of ring 0.25 mm. (0.01 in.). This ring shall be attached in a convenient manner to a No. 13 B. & S. gauge brass wire (diameter 1.83 mm. =0.072 in.). See Fig. 193.

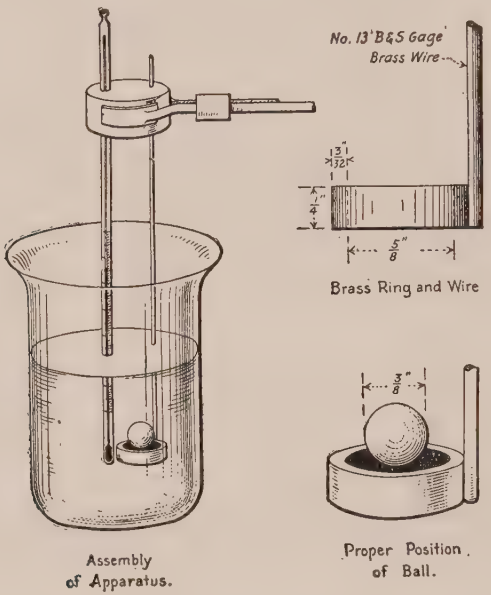


FIG. 193.—Apparatus for Ring-and-Ball Method.

(*b*) A steel ball 9.53 mm. (3/8 in.) in diameter weighing between 3.45 and 3.55 g.

(*c*) A glass vessel, capable of being heated, not less than 8.5 cm. (3.34 in.) in diameter and measuring 10.5 cm. (4.13 in.) in depth from the bottom of the flare. (A 600-ml. beaker, low form, meets this requirement.)

The sample shall be melted at the lowest possible temperature to avoid loss of volatile constituents and stirred thoroughly, avoiding incorporating air bubbles in the mass, and then poured into the ring so as to leave an excess on cooling. The ring, while being filled, should rest on a brass plate which has been amalgamated to prevent the bituminous material from adhering to it. After cooling, the excess material shall be cut off cleanly with a slightly heated knife.

For Substances Fusing at 80° C. (176° F.) or Below.—Use a thermometer which shall be graduated in either Centigrade or Fahrenheit degrees as may be specified, the ranges being −2 to +80° C., or 30 to 180° F., respectively. Fill the glass vessel to a depth of substantially 8.25 cm. (3.25 in.) with freshly boiled, dis-

tilled water at 5° C. (41° F.). Suspend the ring containing the sample in the water so that the lower surface of the filled ring is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel and its upper surface is 5.08 cm. (2 in.) below the surface of water. Place the ball in the water but not on the specimen. Suspend the thermometer so that the bottom of the bulb is level with the bottom of the ring and within 0.635 cm. (¼ in.), but not touching the ring. Maintain the temperature of the water at 5° C. (41° F.) for fifteen minutes.[3] With suitable forceps, place the ball in the center of the upper surface of the bitumen in the ring, thus completing the assembly as in Fig. 193. Apply the heat in such a manner that the temperature of the water is raised 5° C. (9° F.) each minute. The temperature recorded by the thermometer at the instant the bituminous material touches the bottom of the glass vessel shall be reported as the softening point. No correction shall be made for emergent stem. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three shall be ±0.5° C. (0.9° F.). All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

For Substances Fusing above 80° C. (176° F.).—The thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being 30 to 160° C., or 85 to 320° F., respectively. The same method as given above shall be employed, except that U. S. P. glycerin shall be used instead of water, and the starting point of the glycerin bath shall be 32° C. (89.6° F.). The bath shall be brought to this temperature and thoroughly agitated, then the apparatus and specimens shall be placed in the bath which shall be maintained under agitation at the starting temperature for fifteen minutes, after which the assembly shall be completed by placing the ball on the center of the specimen and the test carried on as above. In applying the heat, the ring apparatus shall be placed off the center of the container and the burner placed midway between the center and edge of the beaker away from the specimen.

Rigid adherence to the prescribed rate of heating is absolutely essential in order to secure accuracy of results. A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the bituminous material from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning. The limit of accuracy of the test is ±0.5° C. (0.9° F.).

Cube Method.—This method is restricted to testing tar-pitches, and has been standardized as follows:

The softening of pitch takes place at no definite moment or temperature. As the temperature rises, pitch gradually and imperceptibly changes from a brittle or exceedingly thick and slow-flowing material to a softer and less viscous liquid. For this reason the determination of the softening-point must be made by a fixed, arbitrary and closely defined method if the results obtained are to be comparable.

The apparatus shall consist of the following:

(*a*) A mold suitable for forming a 12.7-mm. (½-in.) cube of pitch. (A recommended type is shown in Fig. 194).

[3] Note by Author.—It will be found more convenient, and the accuracy of test will in no way be sacrificed, if the initial temperature of the water is maintained 25° F. below the softening point of the substance under examination.

(*b*) An L-shaped right-angled hook made of No. 12 B. and S. gauge copper wire (diameter 2.05 mm. = 0.0808 in.) the foot of which shall be 2.54 cm. (1 in.) long.

(*c*) A glass vessel, capable of being heated, not less than 8.5 cm. (3.34 in.) in diameter and measuring 10.5 cm. (4.13 in.) in depth from the bottom of the flare. (A 600-ml. beaker, Griffin low form, meets this requirement.)

(*d*) A thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −2 to +80° C. or +30 to +180° F., respectively.

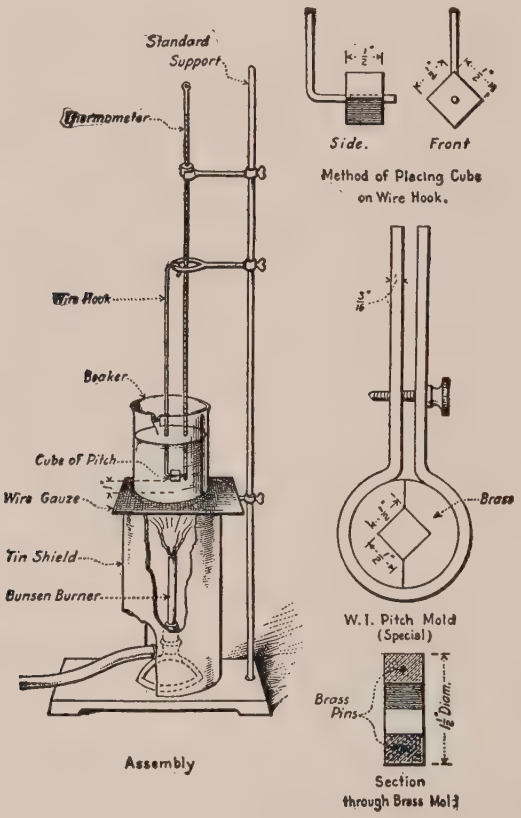


FIG. 194.—Apparatus for Cube-in-Water Method.

The pitch shall be formed into a 12.7-mm. (½-in.) cube, truly shaped and with sharp edges, either by melting and pouring, or softening and pressing, into a mold. In all cases an excess of pitch shall be used and the surplus material shall be cut off cleanly with a slightly heated knife. The harder pitches specified can ordinarily be molded at room temperature, the softer pitches in water at about 4° C. (39.2° F.). If they are melted, they should first be thoroughly stirred, avoiding incorporating air bubbles in the mass, and then

poured into the mold so as to leave an excess on cooling. The mold should rest on a brass plate and the surface of the plate and the interior surfaces of the mold should be amalgamated to prevent the pitch from adhering to them.

For Pitches Fusing between 110 and 170° F.—Assemble the apparatus as shown in Fig. 194. Fill the glass vessel to a depth of substantially 9.5 cm. (3.75 in.) with freshly boiled, distilled water at 15.5° C. (60° F.). Place the cube of pitch on the wire as shown in Fig. 194 and suspend it in the water so that its lower edge is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel and its upper edge is 5.08 cm. (2 in.) below the surface of the water. Allow it to remain in the water for fifteen minutes before applying heat. Suspend the thermometer so that the bottom of the bulb is level with the bottom edge of the cube of pitch and within 0.635 cm. (¼ in.), but not touching the cube. Apply the heat in such a manner that the temperature of the water is raised 5° C. (9° F.) each minute. The temperature recorded by the thermometer at the instant the pitch touches the bottom of the glass vessel shall be reported as the softening-point. No correction shall be made for emergent stem. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three shall be ±0.5° C. (0.9° F.). All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

For Pitches Fusing below 110° F.—Use the same method as given above, except that the water when placed in the glass vessel shall be at a temperature of 4° C. (39.2° F.). The cube shall be allowed to remain fifteen minutes in this water before applying the heat.

The use of freshly distilled water is essential, as otherwise air bubbles may form on the cube and retard its sinking. Rigid adherence to the prescribed rate of heating is absolutely essential in order to secure accuracy of results. A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the pitch from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning. The limit of accuracy of the test is ±0.5° C. (0.9° F.).

For Pitches Fusing above 170° F.—The heating is performed in an air bath in the apparatus illustrated in Fig. 195. The cube should be suspended in line with the observation windows, and the thermometer bulb brought to the same level. The temperature is raised 9° F. per minute, and recorded by the thermometer when the cube drops 1 in.

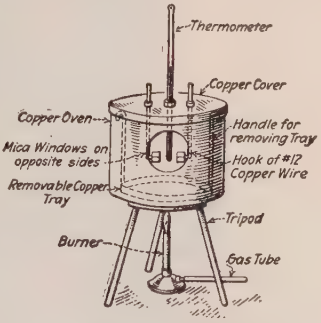


FIG. 195.—Cube-in-Air Method for High Fusing-point Substances.

Volatile Matter

This test is used for identifying various bituminous materials. Thus in the case of asphalts, the volatilization test will often serve to identify soft native asphalts, which contain larger percentages of volatile matter than soft residual or blown petroleum asphalts. Cut-back products also carry a large percentage of volatile constituents.

The test may also be used to determine the adaptability of a bituminous substance for certain definite purposes, where it becomes necessary to heat it to high temperatures, as for example in the paving industry or in manufacturing bituminized roofings and floorings. It likewise serves as a valuable adjunct for gauging the uniformity of supply and for purposes of factory control. It also furnishes an *indication* of the weatherproof properties of the material. Other thing being equal, bituminous substances showing the smallest percentage of volatile matter will prove most weatherproof on exposure to the elements. It should be noted, however, that the volatility test alone must not be taken as the final criterion as to whether or not a bituminous substance is weatherproof, since other factors should also be taken into consideration. The volatility test may be regarded as an accelerated test, showing the loss of volatile constituents exclusive of water which will take place upon exposure to the weather in a relatively thin layer, for a long time.

The following method has been adopted as standard.

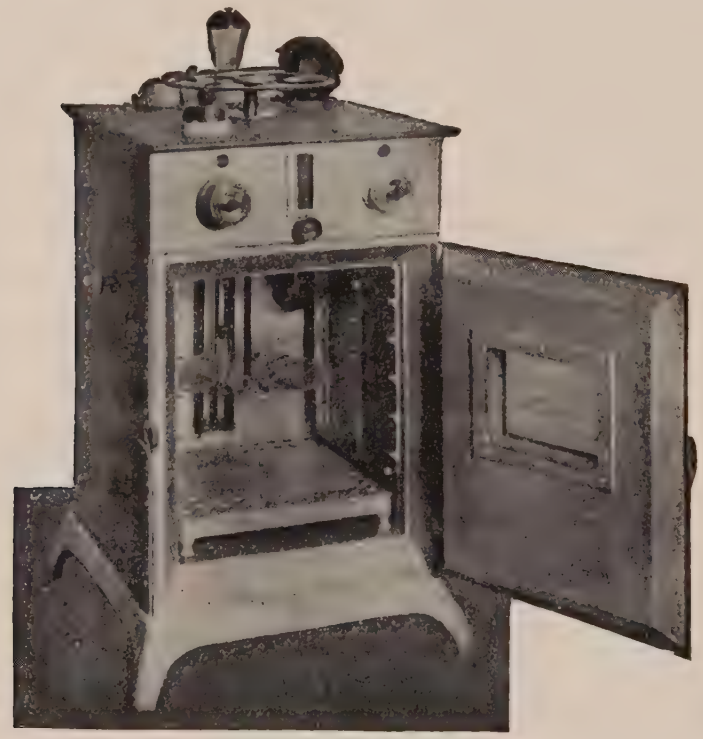


Fig. 196.—Electrically-heated Volatility Oven.

This test covers the determination of the loss in weight (exclusive of water) of oil and asphaltic compounds when heated as hereinafter prescribed. The material under examination shall, therefore, first be tested for water and if water is found to be present, it shall be removed by suitable methods of dehy-

dration before the material is subjected to the loss on heating test; or another sample shall be obtained which is free from water.

The oven shall be rectangular in form with double walls and heated by electricity, as illustrated in Fig. 196. Its interior dimensions shall be as follows: height, exclusive of space occupied by the heating element, not less than 29.26 cm. (11.5 in.), width and depth, each, at least 5.08 cm. (2 in.) greater than the diameter of the revolving shelf. The oven shall be provided with a perforated metal circular shelf approximately 24.8 cm. (9.75 in.) in diameter. A recommended form of aluminum shelf is shown in Fig. 197. This shelf shall

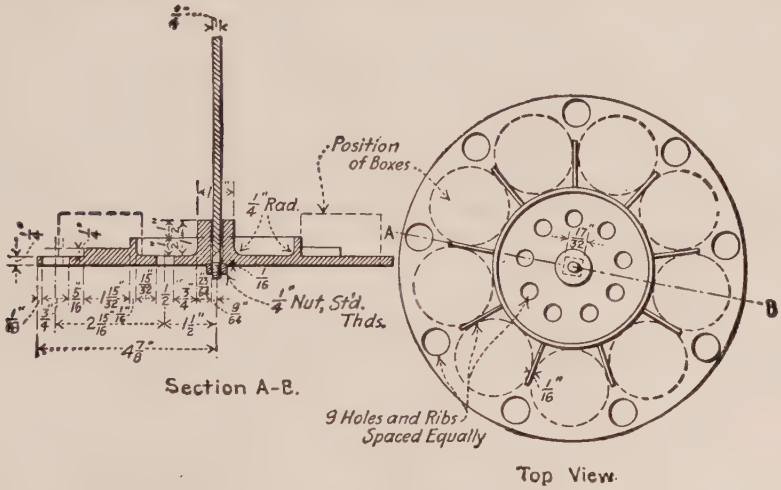


FIG. 197.—Shelf for Volatility Oven.

be placed in the center of the oven, with respect to all dimensions of the interior of the same, suspended by a vertical shaft and provided with mechanical means for rotating it at the rate of 5 to 6 revolutions per minute. One side of the oven shall be hinged and equipped to serve as a tight fitting door which shall contain a window at least 4 in. square, with double glass, through which a thermometer, located in front of and level with the revolving shelf, may be read without opening the door. One round vent hold shall either be placed in the top and bottom of the oven, or one only near the top, and one only near the bottom at each side of the oven. Each hole shall be not less than 1.27 cm. (0.5 in.) nor more than 1.60 cm. (0.63 in.) in diameter and they shall both be left open during the operation of the oven.

The thermometer shall be graduated in Centigrade degrees, the range being 155 to 170° C.

The container in which the sample is to be tested shall be of metal or glass, cylindrical in shape, and shall have a flat bottom. Its inside dimensions shall be substantially as follows: diameter, 55 mm. (2.17 in.); depth, 35 mm. (1.38 in.).

NOTE.—The American Can Company's 3-oz. Gill style flat-bottom, seamless ointment box, deep pattern, fulfills these requirements.

The sample as received shall be thoroughly stirred and agitated, warming, if necessary, to insure a complete mixture before the portion for analysis is removed.

Fifty grams of the water-free material to be tested shall be weighed into a tared container conforming to the foregoing requirements. The oven shall be brought to a temperature of 163° C. (325° F.), and the box containing the sample placed in one of the recesses of the revolving shelf. The oven shall then be closed and the shelf rotated 5 to 6 revolutions per minute during the entire test. The temperature shall be maintained at 163° C. ±1° C. (325° F. ±1.8° F.) for 5 hours after the sample has been introduced and the oven has again reached that temperature. The sample shall be removed from the oven, cooled and weighed, and the loss due to volatilization calculated. During the 5-hour period the temperature shall not vary more than ±1° C. (±1.8° F.). All tests showing a greater variation in temperature shall be rejected.

Under ordinary circumstances a number of samples having about the same degree of volatility may be tested at the same time. Samples varying greatly in volatility should be tested separately. Where extreme accuracy is required, not more than one material should be tested at one time and duplicate samples of it should be placed simultaneously in the oven. Such duplicates shall check within the limits of accuracy given below. Results obtained on samples showing evidences of foaming during the test shall be rejected.

Up to 5% loss in weight, the results obtained may be considered as correct within 0.5. Above 5% loss in weight the numerical limit of error increases 0.01 for every 0.5% increase in loss by volatilization, as follows:

Volatilization Loss, Per Cent	Numerical Correction	True Volatilization Loss, Per Cent
5.0	±0.50	4.50– 5.50
5.5	±0.51	4.91– 6.01
6.0	±0.52	5.48– 6.52
10.0	±0.60	9.40–10.60
15.0	±0.70	14.30–15.70
25.0	±0.90	24.10–25.90
40.0	±1.20	38.80–41.20

NOTE.—If additional periods of heating are desired, it is recommended that they be made in successive increments of five hours each. When the penetration or other characteristics of the sample after heating are required, melt the residue in the container at the lowest possible temperature and thoroughly mix by stirring, taking care to avoid incorporating air bubbles in the mass. Then bring it to the standard temperature and test as prescribed.

Evaporation Test

This test is used principally for testing road oils, in determining the so-called asphalt content, and is carried out by evaporating the specimen under carefully controlled conditions until the residue shows a penetration of exactly 100 at 77° F. (100 g., 5 sec.). The percentage by weight of residue is recorded and furnishes an indication of the quantity of constituents present which may be depended upon to contribute to the durability of the pavement. It will serve to differentiate between straight-distilled and cut-back products. This test has been standardized as follows:

This method of test covers the determination of percentage of residue having a specified penetration at 100 g., five seconds, 25° C. (77° F.), obtained by

heating a road oil or a semisolid asphalt having a penetration of more than 100, at a temperature of 249 to 260° C. (480 to 500° F.). When the penetration of the residue is not otherwise stated it shall be understood to be 100. The residue obtained is available for testing as desired.

This method of test covers the determination of percentage of residue having a specified penetration at 100 g., 5 seconds, 25° C. (77° F.), obtained by heating a road oil or a semi-solid asphalt having a penetration of more than 100, at a temperature of 249 to 260° C. (480 to 500° F.). When the penetration of the residue is not otherwise stated it shall be understood to be 100. The residue obtained is available for tests as desired.

The apparatus shall consist of a container, heating bath, hot plate, and thermometer, with necessary accessory apparatus. The container in which the sample is to be tested shall be a flat-bottom, cylindrical seamless tin box, 70 mm. (2¾ in.) in diameter and 45 mm. (1¾ in.) in depth.

NOTE.—The American Can Co.'s 6-oz. Gill style flat-bottom, seamless ointment box, deep pattern, fulfills these requirements.

(*a*) The heating bath shall be a cast-iron air-bath permitting the immersion of the container to a depth of 1¼ in. through an opening $\frac{1}{16}$ in. larger in diameter

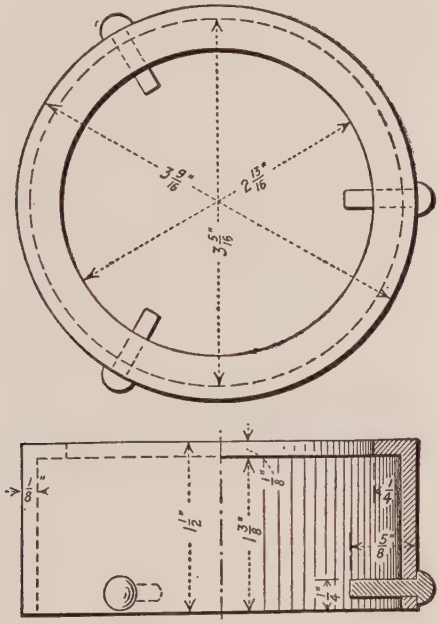


FIG. 198.—Cast-Iron Air-Bath.

than the container. It shall support the container ¼ in. above the hot plate and with at least ¼ in. free air space between the sides of the container and of the air-bath below the opening. A suitable air-bath is shown in Fig. 198.

(*b*) The air-bath shall be heated upon a suitably mounted hot plate, heated either electrically or by means of a gas flame. The plate shall be capable of maintaining the sample continuously at the required temperature, and apparatus necessary to fulfill this requirement, such as a rheostat or gas pressure regulator, shall be provided.

The thermometer shall conform to the following requirements. These specifications cover a special thermometer graduated to either Centigrade or Fahrenheit degrees as specified, the ranges being −6 to +400° C., or +20 to +760° F., respectively. The sample as received shall be thoroughly stirred and agitated, to insure a complete mixture before the portion for testing is removed.

One hundred grams (100.00±0.10 g.) of the material to be tested shall be weighed into a tared container, which shall then be placed in the air-bath in position to be heated. The thermometer shall be supported in the sample equidistant from the sides of the container and with the bottom of the bulb neither more than ¼ in. above nor touching the bottom of the container. The bulb shall be completely immersed in the sample throughout the heating. An assembly of the apparatus is shown in Fig. 199.

Fig. 199.—Assembly of Apparatus for Evaporation Test.

The sample should be heated as rapidly as possible, to prevent foaming, to a temperature of 249° C. (480° F.) and during the evaporation, the temperature shall be maintained between 249° C. (480° F.) and 260° C. (500° F.). The sample shall be stirred with the thermometer from time to time to prevent local overheating and, to maintain a homogeneous sample, all cakes of hardened bitumen which form at the sides of the container shall be fluxed in the sample.

An experienced operator can judge approximately what percentage of residue he should obtain to secure the desired penetration. When it is supposed that the residue will show the required penetration, the bitumen on the

thermometer which may be readily scraped off shall be returned to the container, which then shall be removed from the air-bath, cooled and weighed. The penetration of the residue shall then be determined with the exception that the 6-oz. container in which the evaporation has been conducted, shall be used instead of the 3-oz. container specified in the test for "penetration."

It frequently is necessary to make several trials before a residue of the required penetration is obtained. If it is determined to be greater than that required, all water shall be removed from the container and the surface of the sample, and the heating and determination of penetration may be repeated as before. Ordinarily a residue shall be considered as satisfactorily obtained when its penetration is within 15 of that desired, and its percentage by weight of the original sample shall be calculated. When it is necessary to determine more precisely the percentage of residue having the specified penetration, such a percentage shall be computed by interpolation between percentages of two residues, one having a penetration greater and one having a penetration lower than that specified. The percentage shall be reported as:

Percentage of residue of.....penetration (determined.....) stating, first, the specified penetration, and second, the penetration actually determined for the sample tested or calculated by interpolation.

Certain types of road oil will readily form rings of hard asphalt at the side of the container. Great care should be taken that this material be completely fluxed in the sample before the penetration of the residue is determined. Duplicate determinations should not differ by more than 1.0% with the same operator nor more than 2.5% between different laboratories.

Flash-Point

A number of flash-point testers have been proposed, including the Pensky-Martens, the Cleveland and the Tag types, which are fully described on p. 1744 ff.

Fixed Carbon

The same procedure is followed as for testing coal ("Volatile Combustible Matter"), as described on p. 1638 and p. 1639.

Distillation Test

The value of this test is to ascertain the adaptability of bituminous materials for a given use, generally for road treatment; also for gauging the uniformity of supply, for purposes of factory control, and most important of all, as a criterion of the quality. This test is generally applied to tar products as an equivalent of the volatility test becomes of value in identifying the kind used (upon determining the specific gravity of the fractions distilled), as a means of distinguishing a cut-back tar from a straight-distilled tar (upon determining the specific gravity of the fractions, their viscosity, also the fusing-point of the residue), and for detecting the presence of abnormal amounts of naphthalene.

This test has been standardized as follows:

(*a*) ***For Road Oils (Asphaltic and Coal-tar Pitch), etc.***—The apparatus consists of a flask, condenser tube, shield, receivers and thermometers as specified.

Flask: The distillation flask, Fig. 200, shall be a side neck distilling flask, having the following dimensions:

Diameter of bulb, outside	86	mm. ±1.5 mm.
Diameter of neck, inside	22	mm. ±1.0 mm.
Diameter of tubulature, inside	10.0	mm. ±0.5 mm.
Height of flask, outside	131	mm. ±1.5 mm.
Vertical distance bottom of bulb, outside, to horizontal tangent at tubulature inside	93	mm. ±1.5 mm.
Length of tubulature	220	mm. ±5.0 mm.
Angle of tubulature	73	deg. ±2 deg.
Thickness of tubulature wall	1.0 to 1.5 mm.	

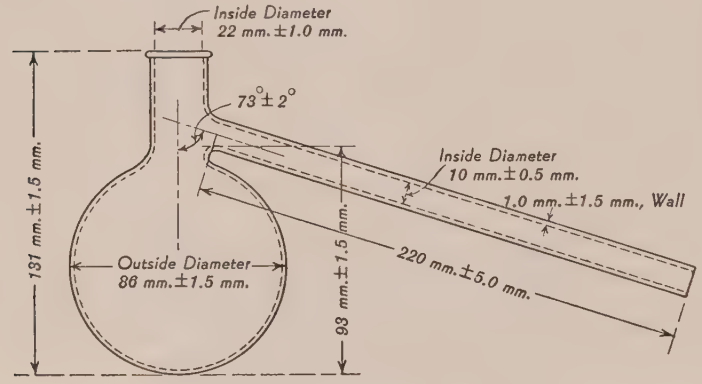


FIG. 200.—Distillation Flask.

Condenser Tube: The condenser tube shall be a suitable form of tapered glass tubing of the following dimensions:

Outside diameter of small end	12.5	mm. ±1.5 mm.
Outside diameter of large end	28.5	mm. ±3.0 mm.
Length	360.0	mm. ±4.0 mm.
Length of tapered part	100.0	mm. ±5.0 mm.

Shield: A galvanized iron shield, lined with ⅛-in. asbestos, of the form and dimensions shown in Fig. 201 shall be used to protect the flask from air currents and to prevent radiation. The cover (top) may be of transite board made in two parts, or it may be of galvanized iron lined with ⅛-in. asbestos.

Receiver: The distillates shall be collected in tared Erlenmeyer flasks having a capacity of 50 to 100 ml.

Thermometer: The thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the range being from 0 to 400° C. or 30 to 760° F., respectively.

The sample as received, shall be thoroughly stirred and agitated, warming if necessary, to insure a complete mixture before the portion for analysis is removed.

The material may be tested for distillation without dehydration, if water is present not to exceed 2.0%. If water is present in excess of 2.0%, the bituminous material shall be dehydrated before testing, by distilling 500 ml.

in an 800-ml. copper still provided with a water-cooled condenser, the distillate being caught in a separatory funnel. When all the water has been ex-

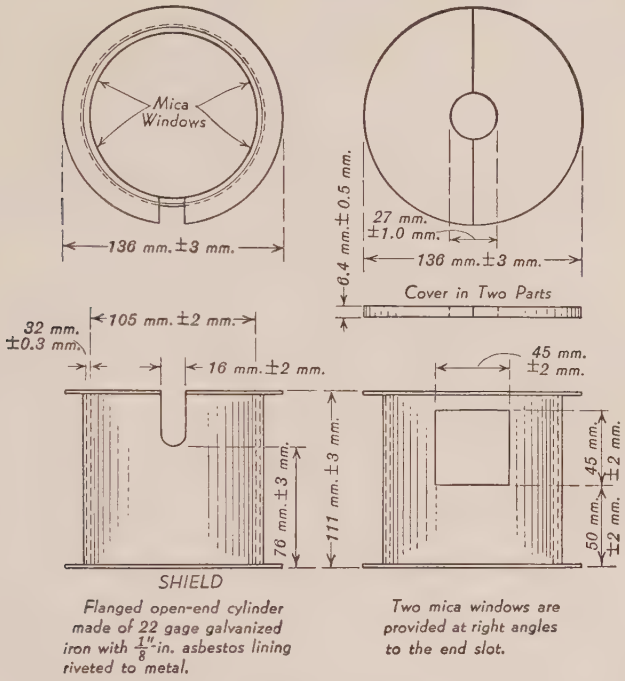

Mica Windows
136 mm. ±3 mm.
6.4 mm. ±0.5 mm.
27 mm. ±1.0 mm.
136 mm. ±3 mm.
Cover in Two Parts
32 mm. ±0.3 mm.
105 mm. ±2 mm.
16 mm. ±2 mm.
45 mm. ±2 mm.
76 mm. ±3 mm.
111 mm. ±3 mm.
45 mm. ±2 mm.
50 mm. ±2 mm.
SHIELD
Flanged open-end cylinder made of 22 gage galvanized iron with 1/8 in. asbestos lining riveted to metal.
Two mica windows are provided at right angles to the end slot.

FIG. 201.—Shield.

pelled, the distillate is allowed to settle, the water drawn off and the oils returned to the residue in the still after the contents have cooled below 212° F.

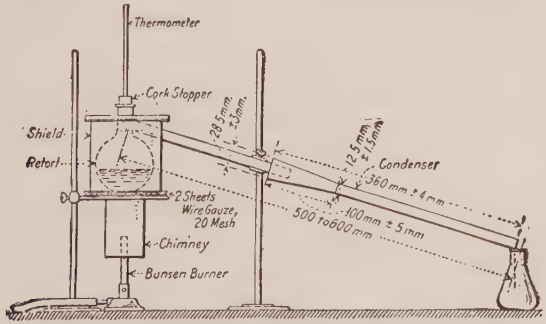


FIG. 202.—Distillation Apparatus Assembly for Road Oils.

The flask shall be supported on a tripod or rings over two sheets of 20-mesh gauze, 150 mm. square, as shown in Fig. 202. It shall be connected to the

condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the neck with the top of the bulb level with the lowest point of juncture of the tubulature and neck of the flask.

The axis of the flask through the neck shall be vertical.

The distance from the bulb of the thermometer to the outlet end of the condenser tube shall be not more than 600 nor less than 500 mm. The burner should be protected from drafts by a suitable shield or chimney.

One hundred grams (100 g. ±0.1 g.) of the sample shall be weighed into the flask, the apparatus assembled and heat applied so that the first drop comes over in from five to fifteen minutes. The distillation shall be conducted at the rate of between 50 and 70 drops per minute and the distillate collected in weighed receivers.

NOTE.—In testing creosote oils: 80 to 120 drops per minute are specified.

The condenser tube shall be warmed whenever necessary to prevent accumulation of solid distillates. The fractions shall be collected at the points designated by the specifications. The receivers shall be changed when the thermometer indicates the maximum temperature for each fraction. When the maximum specified temperature of the test is indicated by the thermometer, the flame shall be removed and any oil which has condensed in the condenser tube shall be drained into the last fraction.

The residue shall remain in the flask with the cork and thermometer in position, until no vapors are visible and it shall then be weighed. If tests of the residue are required, the flask shall then be inclined so that the residue will flow around the sides, thus collecting any condensed vapors that may be on the sides of the flask, after which the residue shall be poured into a suitable receptacle and covered. If the residue becomes so cool that it cannot be poured readily from the flask, it shall be reheated to a temperature not exceeding 125° C. by holding the bulb of the flask in a suitable bath and not by the application of flame. For weighing the receivers and fractions, a balance accurate to at least 0.05 g. shall be used.

During the progress of the distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer. The results of the distillation test shall be reported in percentages by weight of water-free material.

(*b*) ***For Cut-Back Asphaltic Products.***—In testing cut-back asphaltic products, the foregoing method is modified in the following particulars:

The condenser shall consist of a 250-mm. standard glass jacketed condenser (Fig. 203).

The following dimensions are recommended:

Length of jacket, excluding the necks	250	mm. ± 5	mm.
Outside diameter of adapter of condenser tube	23	mm. ± 1	mm.
Length of adapter	75	mm. ± 5	mm.
Outside diameter of condenser tube proper	12.5	mm. ± 0.5	mm.
Over-all length of condenser tube, including adapter	475	mm. ±25	mm.

The adapter shall be of the curved design of heavy wall (1 mm.) and reinforced top glass, with an angle of approximately 105°, and with a diameter at

the large end of approximately 18 mm. The outlet end shall be ground to an angle of 45°±5° with the inside vertical.

The receivers shall be graduated cylinders, of uniform diameter, with a pressed or molded base and a lipped top. The over-all height shall be not less than 24.8 cm. (9¾ in.) nor more than 26.0 cm. (10¼ in.). The cylinder shall

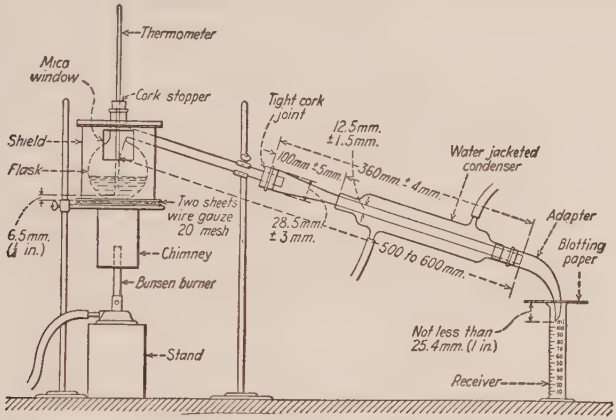


FIG. 203.—Distillation Apparatus Assembly for Cut-Back Asphaltic Products

be graduated in single milliliters to contain 100 ml., and the graduated portion shall be not less than 17.78 cm. (7 in.) nor more than 20.32 cm. (8 in.) in length. Each fifth graduation shall be distinguished by a longer line, and the graduations shall be numbered from the bottom up at intervals of 10 ml. The graduations shall not be in error by more than 1 ml. at any point on the scale.

The flask shall be supported on a tripod or ring over two sheets of 20-mesh gauze, 150-mm. square as shown in Fig. 203. It shall be connected to the condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the neck with the bottom of the bulb ¼ in. from the bottom of the flask. The axis of the flask through the neck shall be vertical. The distance from the neck of the flask to the outlet end of the condenser tube shall be not more than 600 nor less than 500 mm. The burner should be protected from drafts by a suitable shield or chimney.

The adapter shall be adjusted over the end of the condenser tube so as to conduct the distillate into the receiver, and the top of the receiver shall be covered closely during the distillation with a piece of blotting paper or its equivalent, which shall be cut so as to fit the adapter tightly. The adapter shall extend into the receiver at least 2.54 cm. (1 in.) but not below the 100-ml. mark. Unless the laboratory air temperature is between 12.8 and 18.3° C. (55 and 65° F.) the receiver shall be immersed up to the 100-ml. mark in a transparent bath maintained between these temperatures. The condenser tube shall be clean and dry.

Two hundred milliliters (calculated from the specific gravity of the material at 15.5° C. (60° F.)) of the sample shall be weighed into the flask, the apparatus assembled and heat applied so that the first drop comes over in from 5 to 15 min.

The distillation shall be conducted at the rate of between 50 and 70 drops per minute. Should the sample foam the distillation rate will have to be reduced, but the normal rate shall be resumed as soon as possible. If excess foaming persists the distillation may be more easily controlled by applying the flame near the edge of the bulb instead of at the center of same. The distillate shall be collected in the specified receivers, and the volume of distillate at all specified temperatures recorded. The volume of any separated water shall also be recorded. When the maximum specified temperature of the test is indicated by the thermometer, the flame shall be removed and the residue poured *immediately* into a 6-oz. tin box placed on its cover to prevent two rapid cooling at the bottom. Any oil which may remain in the condenser tube shall be drained into the last receiver.

As soon as no further vaporization is apparent, the residue shall be stirred to insure homogeneity, and then poured into the necessary apparatus for the required tests. During the progress of the distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer. Temperatures to be observed in the distillation test shall be corrected for the effect of the altitude of the laboratory in which the test is made.

The results of the distillation test shall be reported in percentage by volume of water-free material.

(*c*) ***For Coal-tar Products.***—In testing coal-tar products, the foregoing method shall be modified as follows: The thermometer shall be inserted through a cork in the neck of the flask, with the bottom of its bulb 12 to 13 mm. from the surface of the oil. The exact location of the thermometer bulb shall be determined by placing a vertical rule graduated in divisions not exceeding 1 mm. back of the flask, when the latter is in position for the test, and sighting the level of the liquid and the point for the bottom of the thermometer bulb.

The following fractions are usually reported:

For Bituminous Road Oils:	For Cut-back Asphalts:	For Coal-tar Products:
Up to 170° C.	Up to 190° C.	Up to 210° C.
170 to 235° C.	Up to 225° C.	210 to 235° C.
235 to 270° C.	Up to 315° C.	235 to 270° C.
270 to 300° C.	Up to 360° C.	270 to 315° C.
Residue.	Residue.	315 to 355° C.
		Residue.

SOLUBILITY TESTS

Solubility in Carbon Disulfide

This test is useful for purposes of identification, for ascertaining the adaptability of a bituminous substance for a given purpose, for gauging its uniformity of supply, and as a criterion of its quality (i.e., purity) and consequently its intrinsic value. Crude bituminous materials are often purchased on the basis of the percentage soluble in carbon disulfide. The presence of non-mineral matter insoluble in carbon disulfide may be regarded as just that much inert material, and in certain cases as an indication that the material has been carelessly prepared or overheated in its process of manufacture. The mineral matter may be regarded as an adulterant. In the case of native asphalts, the larger the percentage soluble in carbon disulfide, the greater will be their intrinsic value. The percentage and composition of the mineral matter will often indicate the source of the native asphalts. Asphalts derived from petroleum are substantially free from mineral constituents, and with the possible exception of the harder grades, contain little to no non-mineral matter insoluble in carbon disulfide.

With a native asphalt containing over 10% of mineral matter, it is necessary to separate the portion soluble in carbon disulfide, before ascertaining its physical characteristics, fusing-point, and sometimes fixed carbon, in which case the soluble constituents should be recovered as will be described.

Two methods will be considered, depending upon whether or not the constituents are to be subjected to a detailed analysis.

Where the Constituents are Not to be Examined Further.—In this case the method recommended follows along the lines of the one standardized by the A. S. T. M. which is substantially as follows, differing however somewhat in phraseology: The sample shall be representative and if it contains more than 2% of water it shall be dehydrated by distillation in a copper still, the water-free distillate being returned to the residue. If the material is hard and brittle, it may be ground [4] and dried at a temperature below the temperature of volatilization of the material, in a shallow nickel or iron dish.

A Gooch crucible, approximately 4.4 cm. in width at the top, tapering to 3.6 cm. at the bottom, with a depth of 2.5 cm. shall be set in the filter tube inserted in the stopper of the filtering flask. The flask shall be connected with the suction pump. Before suction shall be applied, the crucible shall be filled with asbestos [5] suspended in water which shall be allowed to settle partly in the crucible. A light suction shall be applied to draw off the water, leaving a firm mat of asbestos in the crucible. More suspended asbestos shall be added and the process repeated until a felt is built up that barely transmits light. The felt shall then be thoroughly washed with water, dried in a drying oven, and ignited over a Bunsen burner. The crucible shall then be cooled in a desiccator and weighed. An amount of material which shall contain approximately 1 gram of bitumen shall be weighed into a tared Erlenmeyer flask.

[4] Where it is not desirable to crush the rock or sand grains, a lump should be placed in the drying oven until it is heated through and softened at the lowest possible temperature, whereupon it may be crushed into a thin layer and dried as described.

[5] Asbestos (amphibole) cut in pieces not exceeding 1 cm. in length shredded and shaken up with water.

(*a*) ***Method Used Where but Little Finely-Divided Insoluble Matter is Present.***—One hundred ml. of chemically pure carbon disulfide shall be added to the flask in small portions with continued agitation until all lumps disappear and nothing adheres to the bottom. The flask shall be corked and set aside for fifteen minutes.

The Gooch crucible shall be set up again with the suction flask and the carbon disulfide solution carefully decanted through the asbestos felt, with or without light suction as may be found necessary. No sediment shall be allowed to go onto the filter. A small amount of carbon disulfide shall be used to wash down the sides of the flask and then the precipitate shall be brought onto the felt and the flask scrubbed with a feather if necessary to remove all precipitate. The contents of the crucible shall be washed with carbon disulfide until the washings are colorless. Suction shall be applied to the crucible to remove the carbon disulfide. The crucible shall be dried in the oven at 100 to 125° C. for twenty minutes, cooled in the desiccator and weighed.

The weight of the residue in the crucible shall be recorded..... (1)

Ignite the residue in the crucible at a red heat to a clean ash, cool, add a few drops of ammonium carbonate solution, re-ignite to a low red heat, cool and weigh the residue..... (2)

In case any insoluble matter adheres to the flask, it shall be dried, weighed and the increase over the original weight recorded..... (3)

The filtrate containing the soluble matter shall be evaporated, the bituminous residue burned, and the weight of ash recorded..... (4)

Constituents Soluble in Carbon Disulfide equal the weight of material (dry) taken for analysis, minus the sum of items (1), (3) and (4). Calculate this in per cent.

Non-Mineral Constituents Insoluble in Carbon Disulfide equal item (1), minus (2), plus item (3). Calculate this in per cent.

Mineral Constituents equal the sum of items (2) and (4). Calculate this in per cent.

(*b*) ***Method Used Where a Substantial Quantity of Finely-Divided Insoluble Matter is Present.***—This procedure should be followed where the filter clogs unduly, or where the mineral matter passing through the filter exceeds 0.5%. The material should be weighed out in the same way as in the foregoing, and treated with 100 ml. of chemically pure carbon disulfide.

The flask shall be loosely corked and shaken at intervals until all large particles of material have been broken down. The flask shall be left undisturbed for forty-eight hours to permit the contents to settle. The solution shall be decanted into a similar tared flask, care being taken to disturb as little of the residue as possible. The first flask shall be treated again with fresh carbon disulfide as before and left undisturbed for forty-eight hours. The solution from the second flask shall then be carefully decanted upon the Gooch crucible without use of vacuum, and this shall be followed by the solution from the first flask. The filter shall be washed with fresh carbon disulfide. The residue remaining in each flask shall be shaken again with fresh carbon disulfide and allowed to settle for twenty-four hours. The solution from both flasks shall then be decanted through the filter and the residues remaining in the

flasks shall be washed again with carbon disulfide, the solution decanted and the process repeated until the washings are practically colorless. The temperature shall be maintained between 20 and 25° C.

The crucible and both flasks shall be dried at 100 to 125° C. for twenty minutes, cooled in a desiccator and weighed. The procedure from this point on is exactly the same as in the preceding. The per cent constituents soluble in carbon disulfide, non-mineral constituents insoluble in carbon disulfide, and mineral constituents shall be calculated.

The author finds that in the presence of large quantities of finely divided insoluble matter, the method may be materially shortened by adding a weighed quantity (about twice the weight of bituminous material) of freshly ignited, long-fibered amphibole to the bituminous substance in the first flask. On shaking with carbon disulfide, the asbestos serves to dilute the insoluble matter, preventing the latter from clogging the pores of the filter, and accordingly reducing the time of filtration.

Where the Constituents are to be Examined Further.—Extract 25 to 50 g. of the moisture-free bituminous substance with carbon disulfide as previously described, increasing the quantities of carbon disulfide proportionately. In certain cases an extractor described on p. 1568 may be conveniently employed.

Residue Insoluble in Carbon Disulfide: This contains the non-mineral constituents insoluble in carbon disulfide (e.g., insoluble bituminous matter, free carbon and vegetable matter derived from associated soil) together with the mineral constituents retained by the filter (e.g., clay with 2 molecules of water in chemical combination,[6] silica, silicates, calcium and magnesium carbonates, calcium sulfate with half a molecule of water in chemical combination, iron pyrites, etc.). Dry in an oven at 220° F. to constant weight and mix well to obtain a uniform sample. If the mineral matter is coarse, pulverize sufficient of the well-mixed material in a mortar to 200 mesh or finer for use in carrying out the examination described in sections (*a*) to (*e*) inclusive.

(*a*) To determine the water in chemical combination with the clay and calcium sulfate, heat 10 g. to bright redness in a stream of dry hydrogen or illuminating gas, in an electric combustion apparatus, catching the water in a tared calcium chloride bulb, which is reweighed at the end of the operation. The gain in weight represents the water which should be calculated in percentage.

(*b*) To determine the sulfur present in sulfides, weigh 25 g. into a small flask closed with a stopper carrying a thistle tube filled with hydrochloric acid and an outlet tube leading into a beaker of bromine water. Introduce the acid and boil until all the hydrogen sulfide is expelled into the bromine water, which serves to oxidize it into sulfuric acid. Expel the excess of bromine by boiling and precipitate with barium chloride in the usual manner. Calculate the percentage of sulfur present.

(*c*) To determine the carbon dioxide present in carbonates, weigh 1 g. into a Schroetter or Mohr alkalimeter and treat with hydrochloric acid in the usual manner. The loss in weight represents the sum of the carbon dioxide (liberated from the carbonates) and the hydrogen sulfide (liberated from the iron pyrites).

[6] The water of hydration in clay is held tenaciously, for none is given up during one hour's heating at 293° C., although it is expelled on heating to redness.

Subtract the weight of hydrogen sulfide (ascertained in *b*) to arrive at the weight of carbon dioxide present, and calculate its percentage.

(*d*) To determine the non-mineral constituents insoluble in carbon disulfide, weigh 5 g. into a porcelain dish, treat with an excess of concentrated hydrochloric acid, evaporate to dryness on a water bath and then dehydrate the silica by heating in an air-oven at 220° F. for two hours. Boil up with water, filter on a weighed Gooch crucible and wash thoroughly with boiling water until the filtrate no longer shows a reaction for calcium salts. Dry at 220° F. until no further loss occurs and then weigh the residue, which represents the non-mineral constituents insoluble in carbon disulfide, together with clay and its water of hydration, silica, silicates, calcium sulfate and its water of hydration, etc. Ignite to redness until all the carbonaceous matter is consumed and reweigh. The loss in weight represents the sum of the non-mineral constituents insoluble in carbon disulfide, also the total water of hydration (originally associated with the clay and calcium sulfate). Subtract the per cent water of hydration (ascertained in *a*) to arrive at the per cent non-mineral insoluble in carbon disulfide.

(*e*) To determine the iron, aluminum, calcium, magnesium, silica, sulfates, etc., weigh 2.5 g. into a platinum crucible and ignite until all the carbonaceous matter is consumed. Then fuse with potassium-sodium-carbonate, dissolve the melt in water, acidify with hydrochloric acid, evaporate to dryness to dehydrate the silica, take up with boiling water, filter on a weighed Gooch crucible to separate the silica, which is then washed with boiling water until free from salts, ignited and weighed. The filtrate is diluted to exactly 250 ml. at 77° F. whereupon 200 ml. are drawn off, oxidized by boiling with nitric acid, and the iron and aluminum precipitated with an excess of ammonia, filtered, washed, ignited and weighed together as Fe_2O_3 and Al_2O_3. Calcium, magnesium and SO_3 are then determined in the filtrate in the usual manner. The remaining 50 ml. of the original filtrate are then reduced with metallic zinc and sulfuric acid, and the iron titrated with N/10 $KMnO_4$. The Al_2O_3 is then calculated by difference. The percentage of clay present in the original material is calculated from the following formula:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O.$$

Gypsum is calculated from the following formula:

$$CaSO_4 \cdot 2H_2O.$$

Potassium and sodium are determined in a separate portion.

Carbon Disulfide Extract: This contains the soluble bituminous constituents (together with any chemically combined mineral constituents, e.g., iron present in certain asphalts and fatty-acid pitches, lead present in the sludge asphalts, copper present in certain fatty-acid pitches, etc.,)[7] also any colloidal mineral constituents not retained by the asbestos filter (e.g., clay, silica, calcium and magnesium carbonates, etc.). Cool the solution to exactly 77° F., measure its volume and then dilute with carbon disulfide at 77° F. to the next higher 10 ml. mark. Thoroughly agitate the liquid and with a pipette transfer an

[7] It is contended that in natural rock asphalts, a portion of the mineral matter is chemically united with the asphalt in the form of salts of sulfonated acids.

aliquot portion into a tared crucible or dish. Evaporate the solvent over a steam bath, then incinerate the residue and ignite at white heat to a clean ash, until no further loss in weight occurs. Moisten with ammonium carbonate solution, re-ignite at a low heat (not beyond incipient redness) and reweigh. The ash represents the anhydrous clay, silica, calcium and magnesium carbonates, together with the mineral constituents originally in chemical combination with the bituminous matters. Calculate the mineral matter associated with the bituminous constituents in total carbon disulfide extract. Note that any water of hydration originally combined with the clay is not ascertained by the foregoing procedure, but the amount present is usually so small that it may be disregarded without vitiating the results. From the weight of the residue insoluble in carbon disulfide, calculate the soluble bituminous constituents by difference. Evaporate an aliquot portion of the well-mixed carbon disulfide extract to exactly the calculated weight.

It has been found that when the solvent is expelled by heating over a water-bath for one hour, the fusing-point is increased 2 to 3° C.; also that the retention of 1 to 2% of very fine mineral matter does not change the characteristics of the recovered bituminous constituents to any appreciable extent.

The following variations have been proposed for recovering the bituminous constituents in their unaltered state:

(*a*) ***Evaporation at Atmospheric Pressure.***—From the weight of the extracted mineral matter, calculate the bituminous matter by difference, and evaporate the carbon disulfide extract to exactly this weight. This may be conveniently performed by distilling and condensing most of the carbon disulfide over an incandescent light or an electric stove in a large distillation retort connected with a condenser and receiving flask. The retort shall have a thermometer inserted, with the bottom of the bulb approximately 1 in. from the bottom of the retort. The concentrated solution is transferred to a tared dish, evaporated dry on a steam bath with constant stirring, which may be conveniently accomplished with a motor-driven agitator, and the last traces of solvent expelled in an oven at 105° C. until the residue attains the calculated weight.

An alternate procedure consists in distilling the filtered extract (containing a calculated amount of soluble constituents equal to approximately 100 g.) to a bulk of about 150 ml., then transferring the solution to a spherical flask of 300 ml. capacity. The evaporation is completed on a water-bath which is heated from 40° C. up to the boiling-point, at which it is maintained for 5 hours, during which period the contents are stirred at intervals with a tared glass rod. Finally the flask is heated in an electrically heated oil-bath, from an initial temperature of 105° C. to a final temperature of 130° C., which is kept constant for a period ranging from 4 to 6 hours, during which the contents are kept stirred with the tared glass rod. The oil-bath is kept agitated with a motor driven paddle, which likewise causes the flask to revolve. The time of heating in the oil-bath may be determined by dissolving asphalt of known penetration in carbon disulfide and ascertaining the time required at 130° C. to bring its penetration back to its original figure.

(*b*) ***Evaporation under Vacuum.***—The solvent is first removed by distillation as in the foregoing, until the temperature of the residue in the flask reaches 300° F. The distillation flask is then connected to a filter pump and the

distillation continued under a vacuum of 180 mm. mercury, raising the temperature to 500° F. at the rate of 5 to 6° F. per minute. If the original penetration is greater than 150 at 77° F., the distillation temperature should not exceed 425° F. The residue in the flask should then be weighed. This procedure will give satisfactory results, provided the bituminous substance does not contain any appreciable quantity of constituents volatile at 400° F.

The following modification is claimed to give very accurate results. Dissolve the substance in C.P. carbon disulfide previously dried by contact with $CaCl_2$. The extract should contain 5 to 6% of the soluble constituents, and not exceed 240 ml. in volume, which may be attained by evaporation or by dilution. A shallow, circular brass or nickel plate as illustrated in Fig. 204 is

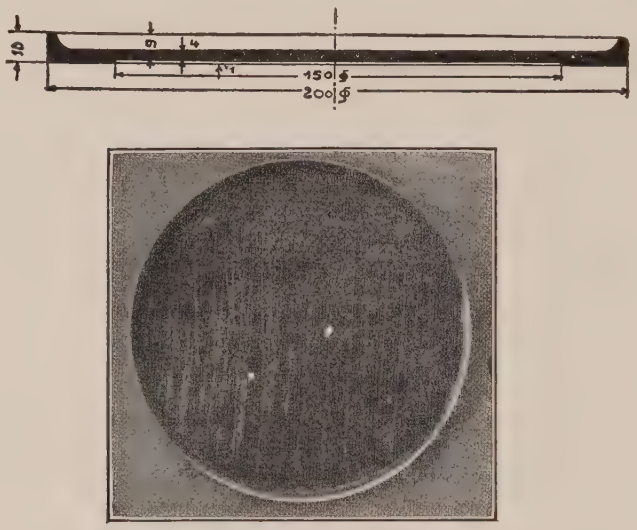


Fig. 204.—Shallow Plate for Evaporation.

supported horizontally (using a spirit level) in a vacuum-dessicator. About 60 ml. of the extract are poured into the plate and distributed uniformly over its bottom, whereupon vacuum is applied to the dessicator (180 mm. mercury) and maintained for 1½ hours. This induces the evaporation of most of the carbon disulfide. Any bubbles or blisters in the residue are pricked with a knife, and the entire layer scratched with the point of the knife in criss-cross directions as illustrated, so as to break it up into ridges, thereby exposing the interior of the mass. It is then evacuated another ½ hour. The plate is then warmed for 10 to 20 minutes at 70° C. in an oven to soften the film of bituminous substance, which is thereupon scraped out with a spatula. Then another 60 ml. of the extract are introduced in the vessel and treated in exactly the same manner. This operation is repeated four times, or until all of the original extract (240 ml.) has been evaporated. In this manner, about 15 to 16 g. of the asphalt is collected and utilized for further tests.

This same method may be adapted to bituminous emulsions, in which case it is modified as follows: About 35 g. of the emulsion are broken by adding a

few drops of concentrated HCl. The separated lumps are freed from acid by kneading in several portions of water with a glass rod. The asphalt is then dissolved in about 240 ml. of carbon disulfide, allowed to stand in a separatory-funnel until most of the water rises to the surface, whereupon the solution is drawn off into a flask and shaken repeatedly with granular $CaCl_2$ at 15 minute intervals. The carbon disulfide solution is then poured off and treated as described above to recover the dissolved asphalt.

(*c*) ***Evaporation in a Stream of CO_2.***—In this case the carbon-disulfide or benzol extract containing 50 to 75 g. of the asphalt is distilled in a wide-mouthed 250 ml. flask in a form of apparatus shown in Fig. 205. The flask is fitted with

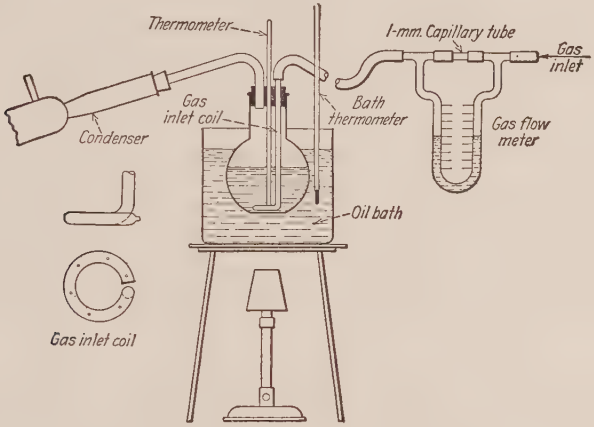


Fig. 205.—Apparatus for Evaporation in Stream of CO_2.

a goose-neck vapor line of approximately 10 mm. internal diameter, connected with a condenser. The CO_2 inlet consists of a copper tube of approximately 5 mm. internal diameter, bent so that its lower end forms a circle slightly less than the diameter of the mouth of the flask, which is perforated with $\frac{1}{32}$ in. holes along its bottom to direct the gas downwardly. A thermometer is inserted through the same cork so that the lower end of its bulb reaches $\frac{1}{4}$ in. from the bottom of the flask and in the center of the circle of the copper tubing. The flask is immersed up to its neck in an oil-bath, which prevents foaming during the distillation. The rate of flow of CO_2 is measured by a differential gage or manometer connected by means of tees to a 1 mm. capillary tube, which is previously calibrated. The gas is drawn from a cylinder through a pressure-regulating valve, and is bled from this through a needle-valve connected to the flow-meter. When the temperature of the asphalt reaches 300° F., the CO_2 is admitted slowly, about 150 ml. per minute, for only a few seconds at a time. This is repeated at 3 to 5° F. intervals and serves to agitate the contents of the flask and minimizes foaming. When the internal temperature reaches 325° F., the gas is admitted at the rate of 875 ml. per minute and held for exactly 15 minutes, whereupon the asphalt should be removed and poured directly into tins or testing molds. A maximum temperature of 300° F. is recommended for asphalts softer than 100 penetration at 77° F.; likewise 350 F.

for asphalts having a fusing-point of over 150° F. (R. and B.). It is important that the extracted asphalt solution be distilled on the same day that it is dissolved, otherwise considerable alteration may occur if the solution is allowed to stand for more than 10 hours, regardless of whether benzol or carbon disulfide is used, and will result in a change in the physical characteristics of the extracted asphalt.

A modification of the procedure consists in distilling off the solvent in a stream of CO_2 under reduced pressure.

A rapid method for separating asphalt from asphaltic limestones and dolomites consists of the following: Weigh out 10 g. of the rock asphalt and add 75 ml. of a mixture of 30 ml. concentrated HCl (sp.gr. 1.19) and 45 ml. ethyl ether. Stir 10 minutes, until the carbonates dissolve; add 75 ml. water and warm over a water-bath until the ether is expelled. Then filter and wash with warm water. Dry the filter at 105° C. and extract the filter with carbon disulfide to recover the asphalt. The extract may be treated by any of the procedures described above.

The soluble bituminous constituents, after being separated in their pure state, as previously described, may be then examined further for their physical and chemical characteristics. Due allowance should be made for the fact that any bituminous matter insoluble in carbon disulfide will be retained mechanically by the extracted mineral constituents, which with asphaltic products is usually relatively unimportant, but in the case of coal-tar products, will amount to a considerable item.

Carbenes

The expression "carbenes" has been applied to that portion of bituminous substances soluble in carbon disulfide but insoluble in carbon tetrachloride. This test is of value in identifying bituminous substances, gauging their uniformity of supply, for purposes of factory control, and as a criterion of their quality. Certain hard native asphalts and asphaltites, particularly grahamite, normally contain a percentage of carbenes, whereas petroleum asphalts do not show carbenes unless they are overheated or over-blown. If more than 0.5% is present in petroleum asphalts, their quality is to be regarded as questionable. Carbenes are found in tars and pitches in varying amounts.

Although carbenes are found in grahamite and certain hard natural asphalts when tested as such, they disappear upon fluxing to a softer consistency. With petroleum asphalts, tars and pitches, the carbenes are of a different character, since they are insoluble in fluxes and do not disappear upon being so treated.

This test is carried out by following the same procedure as in determining the solubility in carbon disulfide, but replacing the latter with carbon tetrachloride. The carbon tetrachloride must be free from carbon disulfide, which may be insured by distilling it under a dephlegmator, discarding any distillate below 76° C. The solvent is then filtered through calcium chloride, and any free hydrochloric acid removed by blowing dry air through it.

The procedure has been standardized as follows:

An amount of material which shall contain approximately one gram of bitumen shall be weighed into a tared Erlenmeyer flask. One hundred milliliters of chemically pure carbon tetrachloride shall be added to the flask in small portions with continued agitation until all lumps disappear and nothing

adheres to the bottom. The flask shall be corked and set aside in subdued light for at least twelve hours.

The Gooch crucible shall be set up again with the suction flask and the carbon tetrachloride solution carefully decanted through the asbestos felt, with or without light suction as may be found necessary. No sediment shall be allowed to go onto the filter. A small amount of carbon tetrachloride shall be used to wash down the sides of the flask and then the precipitate shall be brought onto the felt and the flask scrubbed with a feather if necessary to remove all precipitate. The contents of the crucible shall be washed with carbon tetrachloride until the washings are colorless. Suction shall be applied to the crucible to remove the carbon tetrachloride. The crucible shall be dried in the oven at 100° to 125° C. for twenty minutes, cooled in the desiccator, and weighed.

In case insoluble matter adheres to the flask, it shall be dried and weighed, and the increase in weight over the original weight shall be added to the weight of insoluble matter in the crucible.

The proportion of bitumen soluble in carbon tetrachloride shall be reported on the basis of total bitumen taken as 100:

$$\text{Proportion of Bitumen Soluble in Carbon Tetrachloride.} = \frac{\text{Bitumen Soluble in Carbon Tetrachloride}}{\text{Total Bitumen}}$$

The difference between the percentages soluble in carbon disulfide and carbon tetrachloride respectively, represents the per cent of "carbenes."

Soluble in Petroleum Naphtha

This test is employed mainly for purposes of identification. It is also used to a certain extent for determining the adaptability of bituminous substance for a given use, for gauging the uniformity of supply, and for purposes of factory control. As a general principle, the harder the bituminous product, the smaller will be the percentage that dissolves in petroleum naphtha. Asphaltites are relatively insoluble in this menstruum. Mineral waxes, peat-, lignite- and shale-tars or pitches are largely soluble. The solubility of native and petroleum asphalts varies, depending largely upon their hardness, and also in the case of petroleum asphalts upon the extent to which the distillation has been driven. Coal-tar pitches are relatively insoluble in 88° naphtha.

The portion soluble in petroleum naphtha has been termed "petrolenes" by some, and "malthenes" by others, whereas the non-mineral constituents insoluble in naphtha are generally referred to as "asphaltenes."

It is important that the petroleum naphtha should be derived from petroleum composed entirely of open-chain hydrocarbons, and test exactly 88° Baumé, equivalent to a specific gravity of 0.638 at 60° F./60° F. At least 85% by volume should distill between 95 and 150° F. The density and character of the naphtha is important, since heavy distillates, or products derived from petroleum containing unsaturated or cyclic hydrocarbons, will exert a greater solvent action upon the bituminous substance.

The results will be more consistent if the petroleum spirits is first washed with fuming sulfuric acid to remove the aromatic constituents. There appears to be no difference in the results if the precipitation is carried out at any temperature between 0 and 32° C. As the boiling-point of the petroleum spirits

employed in making the test increases, the quantity of precipitate decreases. The fraction below 105° F. appears to give the most reliable results.

Asphaltenes show increasing solubility in solvents in the order of their surface tension (e.g. ether, benzol, carbon disulfide and pyridine). Ether has been recommended as a substitute for petroleum naphtha, because it is a homogeneous substance, not requiring standardization, and in addition has good flocculating properties and exerts a greater solvent action on hydroxy acids present in certain asphalts.

This method is performed in the same manner as for determining the portion soluble in carbon disulfide, petroleum naphtha being substituted for the latter. Hard bituminous substances should be powdered; liquid bituminous substances flowed in a thin layer over the bottom of the flask; and semi-solid to semi-liquid substances heated until fluid and distributed in a thin layer to present a greater surface to the solvent. It is advisable not to use a stirring rod, as this causes the bituminous substance to adhere to the inner surface of the flask and to the rod itself. The operation should take place at room temperature, and away from the direct rays of the sun. The introduction of a weighed portion of long-fibered asbestos to the solution will assist in its filtration.

The percentage of asphaltenes varies considerably; thus, with asphalts all having the same R. and B. fusing-point of 140° F., the following are obtained: extracted asphalt from Trinidad asphalt 37%, Mexican residual asphalt 20%, California residual asphalt 12%, Colombian residual asphalt 16%, Illinois residual asphalt 12%, Texas residual asphalt 9 to 17%.

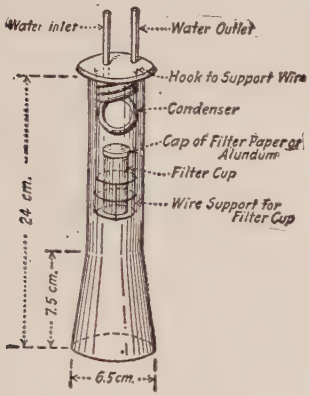
"Free Carbon"

This test is generally used for testing tars and pitches for the presence of non-mineral matter insoluble in hot benzol, although sometimes carbon disulfide is used for the purpose. The test is of value for purposes of identification, for ascertaining the adaptability of the tar or pitch for a given purpose, and for gauging its uniformity of supply. Tars and pitches containing large percentages of insoluble matter, known as "free carbon," are objectionable for certain manufacturing purposes, since the free carbon acts as so much inert matter. The term "free carbon" is a misnomer, since it is not elemental carbon, but a complex mixture of hydrocarbons of high molecular weight, containing 90.0 to 91.7% carbon, 3.4 to 4.0% hydrogen, 1.0 to 1.2% nitrogen, 2.5 to 3.3% oxygen and 0.7 to 1.4% sulfur, on the ash-free basis. The presence of hydrogen has been explained by the great absorptive power of carbon in its pure state, which retains hydrocarbons tenaciously, as well as hydrogen, which is not driven off at temperatures as high as 800° C. Free carbon is more soluble in aniline or pyridine than in benzol or carbon disulfide. Selenium oxychloride exerts the greatest solvent action upon it, but unfortunately the residue cannot be freed from this solvent. It is also partially decomposed by digesting with hot fuming nitric acid.

Marcusson has found that the benzol-insoluble constituents of vertical- and horizontal-retort coal-tars, amounting to 7% and 24% respectively, consisted of oxy-acids 8.6% and 0.5%; pyridine soluble resins 73% and 16.3%; pyridine insoluble resins 18.4% and 32%; and partly coked material 0% and 51.2%

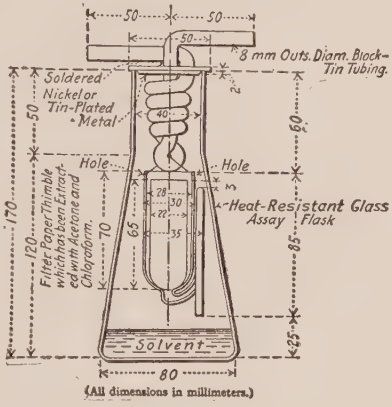
respectively. The following method of extraction should be used. Tars must be dehydrated before extracting, and pitches, if sufficiently hard.

(*A*) ***Porous Thimble Method.***—The extractor shall be of a form shown in Fig. 206, or of a similar form in which the substance is subjected to direct



Courtesy A.S.T.M.

FIG. 206.—Extraction Apparatus.



Courtesy A.S.T.M.

FIG. 207.—Extraction Apparatus.

washing by the vapors of the boiling solvent. The filtering medium shall be a flat-bottom, 30 by 80 mm. RA-98 alundum thimble. The thimble shall be suspended in the extraction flask either by a wire basket hung from two small hooks on the under surface of the metal cover of the flask, or it shall be supported by making perforations near the upper edge of the thimble and suspending from the cover by German silver or platinum wire.

An amount of material which shall contain 10.0 g. $\pm$0.1 g. of the substance shall be weighed into a 100-ml. beaker; 50 ml. of pure benzol shall be added and the solution stirred thoroughly. The solution shall be transferred at once to the weighed alundum thimble. The beaker shall be rinsed clean with pure benzol and the washings added to the thimble. The thimble shall then be covered with a lid of alundum ware and placed immediately in the extraction apparatus. The extractor shall contain a suitable quantity of pure benzol and shall be heated sufficiently to boil the solvent. The extraction shall be continued until the solvent descending from the thimble is colorless. The thimble shall then be dried at 105° C.$\pm$5° C., cooled in a desiccator, and weighed.

(*B*) ***Asbestos Mat Method.***—The filtering medium shall consist of a No. 3 Gooch, Coors porcelain or equivalent crucible approximately 3.5 cm. in diameter at the top, tapering to 2.2 cm. at the bottom with a depth of 4.0 cm., containing a mat of acid-washed medium fiber asbestos approximately 2 mm. in thickness.

The Gooch crucible shall be placed in the suction apparatus and filled with acid-washed medium fiber asbestos suspended in water. Gentle suction shall be applied and more of the suspension, if necessary, shall be added to make a mat approximately 2 mm. in thickness. With the suction still on, the pad shall be washed with water until all small particles of asbestos are removed.

The crucible shall be dried at 105° C.±5° C., placed in a desiccator, and weighed.

An amount of material which shall contain 10.0 g.±0.1 g. of the substance shall be weighed into a 125-ml. Erlenmeyer flask; 50 ml. of pure benzol shall be added and the solution stirred thoroughly and brought to a boil. The hot solution shall be carefully poured into the weighed prepared Gooch crucible without suction until the mat is covered. Then gentle suction shall be applied to the crucible and the remaining solution added, taking care that the mat is covered with solution at all times. The Erlenmeyer flask shall be rinsed clean with pure benzol and the washings added to the crucible. Benzol shall be added to the crucible until the descending solvent is colorless. The crucible shall then be dried at 105° C.±5° C., cooled in a desiccator, and weighed.

(*C*) ***Paper Thimble or Filter-paper Method.***—A paper thimble or else two thicknesses of S. & S. No. 575 or Whatman No. 5 hardened filter-paper (15 cm. in diameter, arranged in cup shape by folding) may be used in connection with an extractor of the form shown in Fig. 207. In this case the procedure is similar to that outlined in the Porous Thimble Method (*A*).

The insoluble residue of "free carbon" includes the mineral ash, which may be ascertained by incineration. Some tars (e.g. blast-furnace tars) contain substantial amounts of ash, which would otherwise introduce serious errors. It has been found that the amount of free carbon will increase with the time the solvent remains in contact with the tar or pitch. The amount of such increase varies with the particular solvent employed. In the case of carbon disulfide or chloroform, the increase is less than with benzol or toluol (or mixtures of these two) and the amount apparently reaches a maximum in about 120 hours.

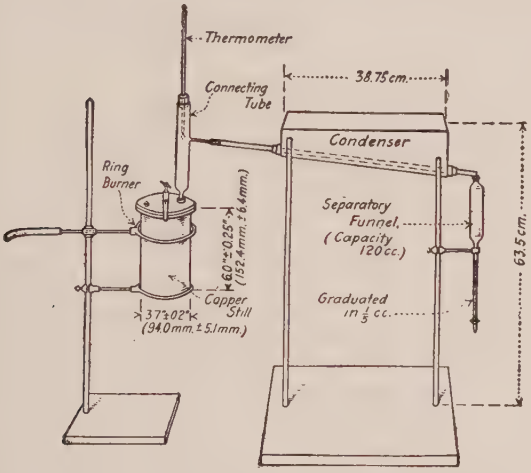
A method has been proposed in which 5 g. of the pitch is heated with 200 ml. tetralin in an autoclave at 240–250° C. under a pressure of 12–13 atmospheres for 2 hours. Upon cooling, the liquid is filtered through a Gooch crucible and washed successively with 50 ml. tetralin and 100 ml. benzol. The residue is dried for 2 hours at 150° C. in an atmosphere of CO_2 and weighed. Anthracene oil (freed from crystallizable substances at 15° C.) has also been proposed, in which case, 5 g. of the substance are digested with 5 g. anthracene oil under a reflux condenser for 4 to 5 hours, cooled, diluted with 500 ml. benzol, filtered, washed with benzol, etc., as in the preceding. Aniline has also been suggested as extracting medium, involving the digestion of 5 g. of substance with 25 ml. aniline over a steam bath for ½ hour, pouring the liquid on a porous clay plate to absorb the solvent, washing the residue with pyridine, followed by benzol, drying and weighing.

CHEMICAL TESTS

Water

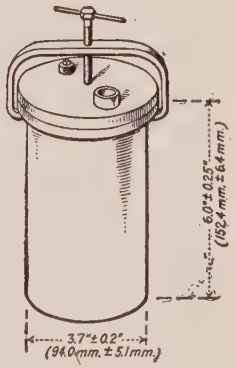
The estimation of water is made in some cases for purposes of identification, and in others as a criterion of the quality. Native asphalts and tars are examined in this way to ascertain whether they exist in the crude or the dehydrated state. This test is also used for dehydrating bituminous substances to render them suitable for further examination, where the presence of water would interfere.

Substances Distilling at Low Temperatures.—This method is adapted to crude petroleum, tars, creosote oil and other fluid bituminous substances distilling at comparatively low temperatures. The apparatus is set up as shown in Fig. 208. The copper still is provided with a removable flanged top and yoke of the form and approximate dimensions shown in Fig. 209.



Courtesy A.S.T.M.

FIG. 208.—Assembled Apparatus for Water Test.



Courtesy A.S.T.M.

FIG. 209.—Copper Still.

The condenser consists of a copper trough carrying a straight-walled glass tube. The separatory funnel has a total capacity of 120 ml. with the outlet graduated in fifths of a milliliter.

Pour 200–500 ml. of bituminous material into the still and weigh. Clamp the top in place, using a paper gasket moistened with lubricating oil. Apply heat with the ring burner supported just above the level of the bituminous material at the beginning of the test, and then gradually lower it as the water distils over. Continue the distillation until the vapor temperature reaches 205° C. Collect the distillate in the separatory funnel, and let it stand until a clean separation of water takes place. Read off the volume of water, calculate its weight, and figure the per cent present in the crude bituminous material.

Draw off the water, and return any light oil to the bituminous matter in the still. The dehydrated material should then be used for further tests.

To prevent frothing and spattering, it has been recommended that the still be surrounded with a cylindrical vessel, closed at the bottom and open at the top, of a somewhat greater diameter than the still. The vessel is so adjusted that its upper rim is a little lower than the level of the bituminous substance in the retort, whereupon it is filled with water until it overflows. Heat is then applied to the shallow layer of tar above the water level, with the ring burner. The water jacket absorbs heat which would otherwise be transmitted to the lower level of the tar and cause bumping. The level of water falls gradually by evaporation, permitting the zone undergoing dehydration to fall slowly. When the water level has fallen below the bottom of the still, the contents are practically dehydrated.

A modification of the foregoing method has been suggested which consists in providing the cover of the copper retort with two openings, one connected with a receptacle holding 100 ml. of tar and provided with a stop-cock to control the flow of tar into the retort. A weighed quantity of tar is introduced into the receptacle and enough run into the retort to cover the bottom, and the remainder is allowed to drip slowly into the retort. This prevents the tar frothing over.

Substances Distilling at High Temperatures.—This method is adapted to asphalts and other bituminous substances comparatively free from volatile constituents, and incapable of distilling without suffering decomposition.

Substances Fusing below 300° F.—When it is desired to determine the percentage of moisture without using the residue for other purposes, a convenient method consists in distilling it with a solvent. The following procedure has been standardized:

The apparatus shall consist of a metal still or glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the still or flask. The trap serves to collect and measure the condensed water and to return the solvent to the still. The type of distilling apparatus used is not an essential feature of this method, but glass has been generally used for petroleum products and the metal still for road materials and tars.

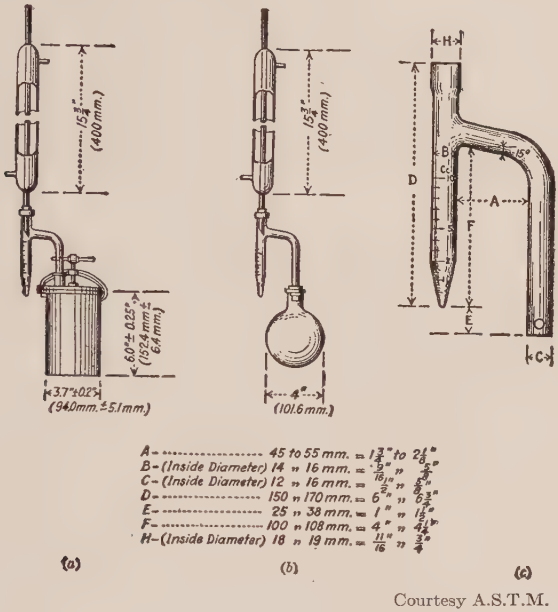
(*a*) The metal still (Fig. 210 (*a*)) shall be a vertical cylindrical vessel, preferably of copper, having a faced flange at the top to which the head is tightly attached by means of a clamp. The head shall be of metal, preferably of brass or copper, and be provided with a tubulation 1 in. in inside diameter.

(*b*) The glass flask (Fig. 210 (*b*)) shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

The burner used with the metal still shall be a ring gas burner 4 in. (100 mm.) in inside diameter. With the glass flask, an ordinary gas burner or electric heater may be used as the source of heat. The condenser shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length with an inner tube 9.5 to 12.7 mm. (⅜ to ½ in.) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30° from the vertical axis of the condenser.

The trap shall be made of well-annealed glass constructed in accordance with Fig. 210 (*c*) and shall be graduated as shown, from 0 to 10 ml. in 0.1 ml. divisions. The error of any indicated capacity shall not be greater than 0.05 ml.

The outside diameters should be preferably 2.5 to 3.5 mm. ($\frac{3}{32}$ to $\frac{1}{8}$ in.) greater than the inside diameters specified.


15½" (400 mm.)
60°±0.25° (1023 mm.±6.4 mm.)
37"±0.2% (940 mm.±5.1 mm.)
15½" (400 mm.)
4" (101.6 mm.)
H
B
C
D
A
F
E
C
A — 45 to 55 mm. = 1¾" to 2⅛"
B — (Inside Diameter) 14 " 16 mm. = ½" " ⅝"
C — (Inside Diameter) 12 " 16 mm. = 15/32" " ⅝"
D — 150 " 170 mm. = 6" " 6¾"
E — 25 " 38 mm. = 1" " 1½"
F — 100 " 108 mm. = 4" " 4¼"
H — (Inside Diameter) 18 " 19 mm. = 11/16" " ¾"
(a)
(b)
(c)

Courtesy A.S.T.M.

FIG. 210.—Apparatus for Water Test.

(*a*) The solvent used when testing petroleum products or bituminous materials derived from petroleum shall be gasoline, free from water, and shall conform to the following distillation requirements:

5% shall distill at a temperature not below 194° F. (90° C.) nor above 212° F. (100° C.)
90% shall distill below 410° F. (210° C.)

(*b*) The solvent used when testing bituminous materials derived from coal tar, water-gas tar, etc., shall be a coal-tar naphtha or a light oil and shall conform to the following distillation requirements:

98% shall distill between 248° F. (120° C.) and 482° F. (250° C.)

The sample shall be thoroughly representative of the material to be tested and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement shall not be permitted.

NOTE.—The difficulties in obtaining proper representative samples for this determination are unusually great so that the importance of sampling cannot be too strongly emphasized.

Procedure: When the sample to be tested contains less than 10% of water, exactly 100 ml. of the material to be tested shall be placed into the still or flask and thoroughly mixed with an equal volume of solvent by swirling, proper care being taken to avoid any loss of material. If the material is measured by vol-

ume, an accurate 100 ml. graduated cylinder shall be used and the contents transferred to the still by rinsing with one 50-ml. portion of solvent, followed by two successive 25-ml. portions of solvent, the cylinder being allowed to drain each time. When the sample to be tested contains more than 10% of water, the volume of material used shall be decreased to that which will yield somewhat less than 10 ml. of water.

NOTE.—In special cases where the water content exceeds 10% and it is not desirable to reduce the size of the sample to that which will yield somewhat less than 10 ml. of water, a distilling tube receiver graduated from 0 to 25 ml. may be used. This tube shall be graduated from 0 to 2 ml. in 0.1 ml., from 2 to 5 ml. in 0.2 ml. and from 5 to 25 ml. in 0.5 ml.

The connections between the still or flask, trap and condenser shall be made by means of tight-fitting corks as shown. The end of the condenser inserted in the trap shall be adjusted to that position which will allow the end to be submerged to a depth of not more than 1 mm. below the surface of the liquid in the trap after distillation conditions have been established. When the metal still is used, a heavy paper gasket moistened with the solvent shall be inserted between the lid and flange before attaching the clamp. A loose cotton plug shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

Heat shall then be applied and so regulated that the condensed distillate falls from the end of the condenser at the rate of from two to five drops per second. The ring burner used with the metal still should be placed about 3 in. above the bottom of the still at the beginning of the distillation and gradually lowered as the distillation proceeds.

The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. This operation usually requires less than an hour. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of distillation for a few minutes.

The volume of condensed water measured in the trap at room temperature multiplied by 100 and divided by the volume of the sample used shall be the percentage of water and shall be reported as "……per cent water by volume, A.S.T.M. method."

The accuracy to be expected with this method is that duplicate determinations of water should not differ from each other by more than one division on the trap.

Substances Not Fusing at 300° F.—In this case the material is comminuted by powdering (to about 60 mesh) or shaving, and a weighed quantity spread in a thin layer on glass and maintained in an oven at 105° C. for one hour, or until the weight becomes constant. If the substance is oxidizable in air, it should be heated in an atmosphere of nitrogen or illuminating gas. Cool in a desiccator, reweigh and calculate the per cent moisture.

Oxygen (in Non-mineral Matter)

There being no satisfactory direct method for determining oxygen, it is computed by subtracting the sum of the percentages of hydrogen, carbon, nitrogen, sulfur, water and ash from 100%. The result so obtained is affected

by all the errors incurred in the other determinations, and especially by the change in weight of the ash-forming constituents on ignition. Iron pyrites will absorb oxygen from the air and change to ferric oxide, increasing the weight of ash, and thereby causing a negative error in the oxygen, equivalent to three-eighths of the pyritic sulfur. Any calcium carbonate present will tend to absorb sulfur combined with the bituminous constituents. On the other hand, there is always a loss on ignition of "water of composition" from the clayey and shaley constituents, also carbon dioxide from carbonates, etc., which tend to compensate for the absorption of oxygen.

A more correct value is obtained by making the corrections indicated in the following formula:

$$\text{Corrected Oxygen} = 100 - [(C - C') + (H - H') + N + H_2O + S' + \text{Corrected Ash}]$$

Where C equals the total carbon; C′ the carbon of carbonates; H the total hydrogen less hydrogen of water; H′ hydrogen from water of composition in clay, shale, etc.; N the nitrogen; H_2O the moisture as found at 105° C.; S′ the sulfur not present as pyrite or sulfate; "Corrected Ash," the mineral constituents originally present, which for most purposes may be calculated with sufficient accuracy by adding to the ash as found, five-eighths of the weight of pyritic sulfur, the CO_2 of carbonates, and the water of composition of clay, shale, etc.

Solid Paraffins

Until recently, it was considered that the presence of paraffin was an indication of the quality of asphaltic products, and many specifications stipulated the maximum percentage permissible. It is now generally conceded, however, that there is no rational relation between the solid paraffins in asphaltic products and their quality. The determination of paraffin is therefore of value only for purposes of identification. Traces of solid paraffins are found in asphaltites, natural asphalts, and in asphalts produced from strictly asphalt-base petroleums. On the other hand, more or less paraffin is present in asphalts derived from non-asphaltic and semi-asphaltic petroleums. It is absent in tars and pitches derived from high-temperature distillation processes.

The following method does not give absolute figures, since it merely discloses the paraffin hydrocarbons which are *solid* at room temperature, without taking the liquid paraffins into consideration; nevertheless the results are of value for purposes of comparison. Weigh 50 g. of the material in a tared 6-oz. glass retort, and slowly distil until nothing but a residue of coke remains. The distillation should take in the neighborhood of forty-five minutes from the time the first drop comes over. The distillation is conducted by heating at the rate of 40 to 50° F. per minute to 450° F., followed by a rise of 15° F. per minute to 500° F. The distillate is caught in an Erlenmeyer flask, and weighed. Either 5 or 10 g. of the well-mixed distillate, depending upon the quantity of solid paraffins present in the crude material, are transferred into a large test tube and dissolved in 25 ml. of absolute ethyl ether and 25 ml. of absolute ethyl alcohol. A similar mixture containing 25 ml. each of ether and alcohol is made up, and this together with the oil solution is cooled separately to exactly

0° F. for one-half hour in a mixture of ice and salt (to which if necessary calcium chloride may be added). The oil solution is then rapidly filtered through a weighed Gooch crucible similarly maintained at 0° F. by a jacket of ice and salt, and washed with 50 ml. of the cooled ether-alcohol mixture. A simple and convenient apparatus consists of an inverted bottle 6 in. in diameter, having the bottom cut off, and attached to the same rubber stopper which supports the funnel holding the Gooch crucible. The space between the bottle, the crucible, and the supporting funnel is packed with the ice and salt mixture. The Gooch crucible is then removed, the outside wiped clean, placed on a tared glass and dried in an oven at 80° C. until the last traces of ether and alcohol are evaporated. The residue is weighed, and the percentage of solid paraffins calculated in the original 50 g. of substance taken for analysis.

Various substitutes have been suggested for the ether-alcohol mixture, including methyl-ethyl-ketone (butanone) containing 1.3% water, having a specific gravity of 0.812 at 20° C.; also nitrobenzene used at 32° C.

It is a mooted question whether the solid paraffins ascertained by the foregoing method are originally present as such in natural asphalts and asphaltites, or are generated during the distillation process through the destructive decomposition of other non-paraffinic components.

An alternate method used with success by the author consists in dissolving 10 g. of the substance in the smallest amount of benzol, applying heat if necessary, adding 200 ml. of warm 88° naphtha, filtering through dried fuller's earth and washing with additional warm 88° naphtha until the filtrate is clear. This removes the dark-colored asphaltic substances, which remain adsorbed by the fuller's earth. The filtrate containing the paraffin is distilled to a small bulk, evaporated to dryness on the water bath under reduced pressure, the residue dissolved in 25 ml. of ether and 25 ml. of alcohol, and treated as described above.

Instead of removing the dark-colored asphaltic constituents by means of fuller's earth, an alternate procedure consists in extracting them by shaking the 88° naphtha solution three successive times with 20 ml. concentrated sulfuric acid in a separatory funnel, followed with N KOH (in 50% alcohol-water solution) and finally with water until neutral to phenolphthalein.

Another method for separating paraffin wax from petroleum residues consists in mixing the residue with an excess of fuller's earth, *cooling* and extracting either with: (1) *cold* benzol (which removes both the oily matters and the asphalt), or (2) *cold* gasoline (which removes the oily matters only) and then with *cold* benzol (which removes the asphalt). The residue of fuller's earth is then treated with *hot* water which separates the adsorbed paraffin wax. This procedure is precisely the reverse of the preceding, which may however be explained by the fact that in this case the process is carried on *in the cold.*

According to Holde, the *refractive index* of the solid paraffins will indicate whether the original substance was ozokerite or paraffin, or a mixture of the two. When tested at 90° C. on the Zeiss or Abbe refractometer, ozokerite will show a refractive index below 15.0, whereas the solid paraffins derived from petroleum, shale, lignite, etc., will test between 15.0 and 30.0. When tested in the solid state, commercial paraffin waxes show a refractive index ranging from 1.500 to 1.540 at temperatures between 30° and 130° F. Furthermore,

paraffin wax has a lower molecular weight than ceresine or ozokerite—for melting points between 50° and 60° C., the former tests between 330 to 400, and the latter above 450.

Sulphonation Residue

(*A*) ***Sulfonation Residue Insoluble in Concentrated Sulfuric Acid.***—This method of test has been proposed for separating saturated and unsaturated hydrocarbons, as a means of destinguishing various asphaltic products (e.g. native asphalts and petroleum asphalts) from tars and pitches, thereby serving for purposes of identification. Two alternate procedures are available, viz.:

(*a*) *Portion Soluble in 88° Petroleum Naphtha.*—The portion soluble in 88° petroleum naphtha is brought to exactly 100 ml., either by adding more 88° naphtha or else by evaporation, so that the quantity of substance carried in solution will be approximately 5 g. This is then shaken in a 500-ml. separatory funnel at 77° F. for *exactly* three minutes, with 30 ml. of a mixture of concentrated sulfuric acid and fuming sulfuric acid, having a specific gravity of 1.84 at 77° F. The funnel is allowed to stand quietly overnight, whereupon the acid is drawn off and the oils unacted upon treated with another 30 ml. of the acid. This time a few hours' standing should effect a sharp separation. If the second acid layer is strongly colored, the treatment should be repeated a third time. The naphtha solution is washed successively with water, a 5% solution of sodium carbonate and finally with water. The solution is evaporated to dryness over a steam bath and the residue weighed. This is equal to the saturated hydrocarbons present in the portion soluble in 88° petroleum naphtha. As a guide in evaporating the last traces of naphtha from the saturated hydrocarbons, a blank test should be run on 100 ml. of the 88° naphtha, whereupon the portion unacted upon is mixed with 0.75 g. of a non-asphaltic petroleum residuum and evaporated on the steam bath alongside of the sample under test, until the former is reduced to exactly its original weight.

The results are expressed as the percentage of saturated hydrocarbons present in the portion soluble in carbon disulfide. This is calculated in the following manner: If a represents the percentage soluble in carbon disulfide, b the percentage soluble in 88° naphtha and c the percentage of saturated hydrocarbons in b; then the saturated hydrocarbons present in the portion soluble in carbon disulfide will equal $(bc/a) \times 100$.

(*b*) *Distillate at 315°–355° C.*—This test expresses the percentage of saturated hydrocarbons in the distillate between 315° and 355° C. obtained upon subjecting the bituminous substance to the flask method of distillation. It is used to differentiate tars and pitches among themselves as well as from mineral waxes, asphalts (native and pyrogenous) and asphaltites. The figures for coal-tar pitches have already been given. The author cites the following additional figures: wood-tar pitch 0%, saponifiable fatty-acid pitches 0%, unsaponifiable fatty-acid pitches 0%, residual asphalt from Mexican asphaltic petroleum 86%, wurtzilite asphalt 87% and gilsonite 85%.

The method of determining the sulfonation residue consists in distilling sufficient of the material under examination by the flask method to obtain at least 10 ml. of distillate between 315° and 355° C. Exactly 10 ml. of this fraction are measured into a Babcock milk bottle, and 40 ml. of 37 normal

sulfuric acid added, 10 ml. at a time. The bottle and its contents are shaken for two minutes after each addition, and when all the acid has been added, the bottle is kept at a constant temperature of 98°–100° C. for one hour, during which it is shaken vigorously every ten minutes. At the end of the hour, the bottle is removed, cooled, filled to the top of the graduations with ordinary sulfuric acid, and whirled for five minutes in a Babcock separator. The unsulfonated residue multiplied by 2 gives the per cent by volume directly (each graduation being equal to 1/200 ml.).

It is important that the acid should be of the proper strength. A mixture of fuming sulfuric acid and ordinary concentrated sulfuric acid should be prepared to contain exactly 80.07% of SO_3, which constitutes 37 normal acid. If the sulfonation residue is dark in color, it should be treated with an excess of a 10% sodium hydroxide solution, and if completely soluble in this reagent, the test is regarded as negative.

(*B*) ***Sulfonation Residue Insoluble in Water.***—Treat 3 g. of the carbon disulfide or benzol soluble portion of the substance, after evaporation of the solvent, with 6 ml. of concentrated sulfuric acid (95%) in a stout test-tube and agitate continuously for three-quarters of an hour while heating in boiling water. The contents of the test-tube are then poured into 500 ml. of cold water. Brown-coal tar and brown-coal-tar pitch are practically insoluble in cold water and partly soluble in hot water. Coal-tar pitch, wood-tar pitch, oil-gas-tar pitch and naphthol pitch are completely soluble in cold water, forming a deep black solution, which upon filtering leave little to no residue. Lignite-tar pitch, peat-tar pitch, bone-tar pitch, rosin pitch, fatty-acid pitch, wool-fat pitch and montan pitch are partly soluble in cold water. Asphalts (both natural, as well as those derived from petroleum) and asphaltites are insoluble in cold water, forming a copious insoluble precipitate. Let the solution stand for two hours and without agitating the precipitate, decant carefully through a weighed Gooch crucible of about 7 cm. diameter. Wash the residue with hot water, and finally transfer the precipitate to the filter. Continue washing with water until the filtrate no longer gives an acid reaction with methyl orange, then dry at 105° C. and weigh. Marcusson used this method for determining the percentage of coal-tar pitch in admixture with refined Trinidad asphalt. He found that upon treating the CS_2 soluble portion of this asphalt with sulfuric acid as outlined above, a small amount of soluble sulfo-derivatives were formed, so that an average correction of 4% must be made to obtain accurate figures.

The foregoing test has been modified for the ostensible purpose of yielding more accurate results, as follows: 2 g. of the substance are weighed in a test-tube 3.5 cm. in diameter, which is immersed 12 cm. in a 30% solution of salt, maintained at 107–108° C., whereupon 20 g. of concentrated sulfuric acid (95%) are added. A mechanical glass stirrer is introduced and caused to revolve at the rate of 300 turns per minute and the digestion continued for 2½ hours. The mechanical stirring is claimed to break up the lumps and result in a better filtration. Carefully introduce water in the test-tube, to a point 12 cm. from the bottom, and continue the stirring for another 15 minutes, then transfer the contents of the tube into 1 liter of boiling water. Let stand over night and carefully filter through two layers of tared filter paper into a 9 cm. porcelain filter, using suction. Wash the residue with boiling water until the filtrate is

clear and no longer reacts acid with methyl orange. The filter containing the residue is placed on a Petri dish and dried for 2 hours at 105° C., cooled in a dessicator and weighed. This represents the asphaltic constituents present, which, however, are contaminated with a certain proportion of *insoluble* sulpho-derivatives of the asphalt. An examination of a range of petroleum asphalts, as well as Trinidad asphalt, indicated that the weight of insoluble asphaltic constituents with their associated insoluble sulfo-derivatives, as ascertained by this method, must be corrected by deducting 20%, to obtain the net weight of asphaltic constituents actually present. Similarly, an examination of a number of coal-tar pitches showed that in no case was more than 0.1% of insoluble sulfo-derivatives present. No correction need therefore be made for pitches. Any free carbon present in the pitch (ascertained by the insoluble matter separated upon originally dissolving the substance in carbon disulfide) should be taken into account by using the following formula:

$$\% \text{ Asphalt} = 80\%(100 - C) \cdot \frac{S}{E}$$

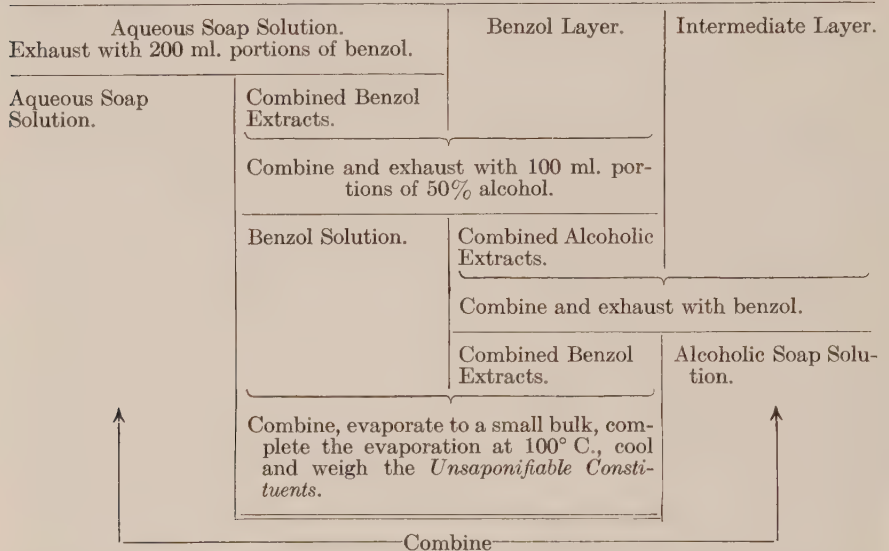
where: C = percent free carbon present in the mixture; S = grams residue obtained after sulfonation; E = grams mixture (after having been freed from insoluble constituents and carbonaceous matter) taken for the sulfonation process.

Saponifiable Constituents

Certain bituminous substances, such as montan wax, rosin pitch, and fatty-acid pitch, are often composed largely of saponifiable constituents. Others, including pine tar, pine-tar pitch, hardwood tar, hardwood-tar pitch, peat tar, lignite tar, bone tar, bone-tar pitch and other forms of fatty-acid pitches, contain smaller percentages. This test is also used for gauging the uniformity of supply, and in the case of fatty-acid pitches, as a criterion of the quality.

The following procedure has been devised by the author for specifically examining bituminous materials or admixtures of bituminous materials with animal or vegetable oils and fats, since the customary methods do not adapt themselves especially well, due to the formation of troublesome emulsions. The bituminous material is first freed from insoluble constituents, including any mineral matter, by boiling with benzene under a reflux condenser, cooling and filtering through a Gooch crucible. The insoluble constituents are dried at 100° C. and weighed. Sufficient of the bituminous substance should be taken to yield approximately 5.0 g. of extract. The benzene solution is evaporated or distilled to 50 ml. and 50 ml. of the saponifying liquid added from a pipette. This should consist of a 10% solution of caustic potash, prepared by dissolving 100 g. of anhydrous potash in 500 ml. of 95% ethyl alcohol, and diluting to a litre with 90% benzene. The liquid is allowed to stand overnight to permit any carbonate to settle, and the clear solution decanted. After the saponifying agent is added, the mixture is boiled under a reflux condenser, for ½–1 hour, and the contents of the flask while still warm poured in a separatory funnel containing 150 ml. of boiling water and 25 ml. of a 10% solution of potassium chloride. Add 250 ml. of benzene, agitate vigorously, and allow the funnel to rest quietly in a warm place until the solvent separates. If an emulsion forms which refuses to separate on standing, add 200 ml. more benzene and 100 ml. 95% ethyl alcohol and stand in a warm place overnight. This will invariably effect a more or less complete separation of the solvent. From this point on the method is illustrated by the following tabular outline:

Saponify as described.
Draw off the soap solution as completely as possible.
Decant the benzol layer, leaving the intermediate layer in the separatory funnel.


Aqueous Soap Solution. Exhaust with 200 ml. portions of benzol.
Benzol Layer.
Intermediate Layer.
Aqueous Soap Solution.
Combined Benzol Extracts.
Combine and exhaust with 100 ml. portions of 50% alcohol.
Benzol Solution.
Combined Alcoholic Extracts.
Combine and exhaust with benzol.
Combined Benzol Extracts.
Alcoholic Soap Solution.
Combine, evaporate to a small bulk, complete the evaporation at 100° C., cool and weigh the Unsaponifiable Constituents.
Combine

Transpose with dilute hydrochloric acid, warm and exhaust with benzol. Separate the aqueous solution containing the glycerol and mineral salts. Evaporate the combined benzol extracts to a small bulk, and then complete the evaporation of solvent at 100° C. Cool and weigh. Weight equals the *free acids derived from the saponifiable constituents.*

In the case of bituminous materials that are more or less completely saponifiable, the intermediate layer is apt to be absent. In this case the process will simplify itself considerably. The foregoing procedure will separate the unsaponifiable constituents in practically an ash-free state.

Diazo Reaction

This test is used for identifying bituminous substances carrying phenols, including wood tar and wood-tar pitch, oil-gas- and water-gas-tars and pitches, shale tar, peat- and lignite-tars and pitches, bone-tar, bone-tar pitch and the various coal-tar pitches.

This reaction is carried out by boiling 2 g. of the bituminous substance with 20 ml. N. aqueous caustic soda, for approximately five minutes. After cooling, the liquid is filtered. If the filtrate is dark colored, it may be lightened by shaking with finely pulverized sodium chloride and filtering. It is then cooled in ice to 10° C., and a few drops of freshly prepared diazobenzolchloride solution added (prepared by dissolving 1 g. aniline chlorhydrate in 10 ml. water and 3 ml. 25% hydrochloric acid, and then adding drop by drop, a saturated solution of 0.5 g. sodium nitrite in water). To avoid the preparation of diazobenzolchloride (which does not keep), the use of paradiazobenzol-sulfonic acid ($C_6H_4 \cdot N_2SO_3$) may be substituted, since it is a more stable chemical and will keep well

in stock. If phenols are present, a more or less fugitive red coloration will result, sometimes accompanied by a reddish precipitate.

Assuming that the bituminous substance gives the diazo reaction, the question will often arise whether the product is a straight-distilled pitch, or an asphalt "cut-back" with a high boiling-point distillate containing phenolic bodies, derived from coal tar, lignite tar, etc. Marcusson has worked out a method applicable under these circumstances, which consists in dissolving 10 g. of the bituminous substance in 15 ml. of benzol, and pouring the solution into 200 ml. of 88° petroleum naphtha. The resulting precipitate is filtered and washed with petroleum naphtha and dried. It is then boiled for fifteen minutes with N/2 alcoholic caustic potash under a reflux condenser to extract the phenols. The liquid is cooled and filtered, the alcohol evaporated, and the residue dissolved in water. Sodium chloride is added to clarify the liquid and remove any substances imparting a dark color, the solution is filtered and the filtrate treated for the diazo test described above. If a straight-distilled pitch containing phenols is present, a positive reaction will be obtained. If the original substance gives the diazo test, but the residue treated in the above way does not, then the admixture of high boiling-point oils containing phenolic bodies with a substance free from phenols (e.g., asphalts, etc.) is established. It is claimed that the presence of as little as 10% of pitch containing phenols may be detected in this manner.

Where bituminous substances contain calcium carbonate, the phenolic bodies present combine with the lime, forming insoluble calcium phenolate which yields but a faint diazo reaction. However, on treating such substances with a solvent in the presence of hydrochloric acid, the calcium phenolate is decomposed, and the diazo reaction becomes much more delicate.

A still more sensitive test for ascertaining the presence of phenols (e.g. tars or pitches) in asphalts consists in the following: A reagent is prepared by dissolving 0.2 g. paranitraniline in 20 ml. water and 5 ml. 20% sulfuric acid, whereupon 0.3 g. sodium nitrite are added. Hard asphalts (3 to 4 g.) are ground in a mortar with 25 ml. water made alkaline with NaOH; then filtered and the filtrate acidified with H_2SO_4 and 3 drops of the foregoing reagent added. The solution is finally made alkaline with NaOH, whereupon the presence of phenols will develop a more or less intense red coloration. It is claimed that the presence of 1% of tar or pitch may thus be detected, inasmuch as a 1 : 25,000 solution of phenol will produce a blood-red color, and a 1 : 250,000 solution a pinkish-red color. Pure asphalts, on the other hand, yield a light yellow color or leave the reagent unchanged.

The Dutch Standardization Committee have adopted a combination of paradiazobenzol-sulfonic acid with Millon's reagent for detecting the presence of phenols in substances containing colophonium, as follows: 10 g. of the substance are boiled 20 minutes with 25 ml. N aqueous NaOH and filtered. To 5 ml. of the filtrate add a few drops of paradiazobenzol-sulfonic acid. If no red coloration results, phenol (tar or pitch) is absent, but if a coloration occurs, tar or pitch may be present, but it may also be caused by colophonium. In this event, the remainder of the filtrate is almost neutralized with nitric acid and evaporated to 5 ml. Then add 5 ml. freshly prepared Millon's reagent and place in a glass beaker with boiling water. If no coloration results within half an hour, the mixture is free from phenols.

Anthraquinone Reaction

The anthraquinone reaction is used for detecting anthracene in tar products produced at high temperatures, including oil-gas-tar and pitch, water-gas-tar and pitch, and the various coal-tar pitches. This test is therefore valuable for purposes of identification.

The tar or pitch is first subjected to distillation in accordance with the retort method, the offtake and condensing tube being kept warm to prevent the accumulation of any solid distillate. The distillate passing over between 270° and 355° C. is caught separately and examined for anthracene in the following manner. The fraction is heated until it is thoroughly fluid to secure a uniform sample, and 5 g. weighed out, while hot. After cooling, 10 ml. of absolute ethyl alcohol are added, the solids allowed to crystallize and the liquid decanted. One to 2 g. of solid substances containing the anthracene are dried on a water-bath, transferred to a 500-ml. flask connected with a return condenser, 45 ml. of glacial acetic acid added, and the contents boiled for two hours. The following mixture is then added drop by drop through a separatory funnel, viz.: 15 g. of anhydrous chromic acid dissolved in 10 ml. of glacial acetic acid, and 10 ml. of water. The boiling is continued for another two hours, the flask cooled, and 400 ml. cold water added. This treatment oxidizes the anthracene to anthraquinone, which on cooling separates as a solid mass. This is filtered, washed with hot water, then with a hot 1% solution of caustic soda and again with hot water. The residue of anthraquinone is then dried and its weight multiplied by 0.856 to obtain the corresponding weight of anthracene. From 0.25 to 0.75% of anthracene is found in coal tars, and a correspondingly larger percentage in coal-tar pitches.

A color reaction for establishing the presence of anthracene consists in boiling for ½ to 1 hour the crystals of anthraquinone (1 part) with zinc dust (2 parts) and 50% NaOH solution (30 parts), whereupon an intense red-colored solution is obtained, which on filtering in contact with air becomes decolorized.

PART II

EXAMINATION OF BITUMINOUS SUBSTANCES COMBINED WITH DISCRETE AGGREGATES

(A) PHYSICAL TESTS OF FINISHED PRODUCT

Resistance to Displacement

This test has been proposed for examining fine-aggregate paving mixtures (e.g. the wearing-course of sheet-asphalt pavements) and has also been adapted for testing coarse-aggregate paving mixtures. The procedure when testing fine-aggregate mixtures consists in weighing the dry sand and filler to 0.1 g.; heating to 350° F. and mixing thoroughly. The melted asphaltic binder heated to 350° F. is then weighed to 0.1 g. and thoroughly mixed with the aggregate by means of a spatula. Approximately 100 g. of the completed mixture are weighed into a cylindrical forming mold 2-in. in diameter and 4-in. high. The mold and contents are heated to 250–260° F. as determined by the thermometer used for stirring the mixture. Remove and insert a cylindrical plunger into

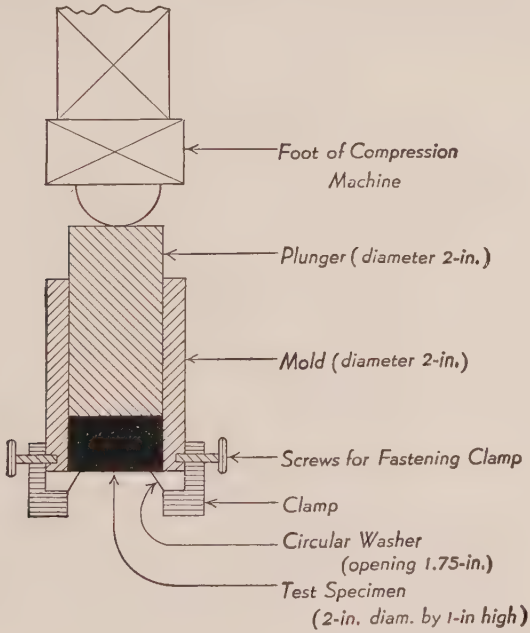


FIG. 211.—Apparatus for Testing Resistance to Displacement.

the mold, and then tamp by first giving 60 blows with a tamper weighing 500 g., followed by 15–20 blows with a tamper weighing 1400 g. The mold and contents are placed in a compression machine to which is applied a load of 3000-lbs.

per sq. in. and the briquette allowed to cool under pressure. The compressed briquette should measure 2-in. in diameter and approximately 1-in. in height. Let stand at room temperature over night and then maintain in a water-bath at 140° F. for one hour before testing. Two such briquettes should be prepared, each specimen being tested by placing it top end down in the testing mold and inserting the plunger as illustrated in Fig. 211. A circular washer having a circular opening 1.75 in. in diameter is clamped on the lower end of the mold and the load then applied at a rate which will cause the testing head to be depressed 1-in. in 25 seconds. As the pressure increases, the briquette will be forced through the orifice of the circular washer. The reading is observed on a spring dynamometer and the maximum is recorded. The average of two specimens is taken as a measure of the "stability" of the mixture. This test indicates the resistance of the pavement to displacement and may be used to proportion mixtures of sand, filler and asphaltic cement giving optimum results.

For testing coarse-aggregate paving mixtures a larger mold is recommended in conjunction with a testing ring $\frac{3}{8}$ in. thick having a minimum orifice $5\frac{3}{4}$ in. in diameter for a depth of $\frac{1}{8}$ in., after which it tapers out to a diameter of 6 in. at the bottom of the ring.

Samples of the finished mixture taken from the testing-plant are warmed to 250°–260° F. and formed into briquettes as described above. Finished pavements may be tested by cutting out cores 2 in. in diameter and approximately $1\frac{1}{4}$ in. high, which are then placed directly in the mold and tested at 140° F.

Tensile Strength

Any standard testing machine may be used provided it is accurate to within 1% of the lowest load to be applied. Special specimen holders of steel, as shown by Fig. 212 (*a*), shall be used. The specimen holders shall be attached to the heads of the machine by links held so that the pull is central, to avoid any transverse strain. For hot-molded materials and for plastic cold-molded materials, the test specimen shall be molded to the form and dimensions shown in Fig. 212 (*b*).

Note.—To permit the use of one mold for all molding compounds the following variations in dimensions of the test specimen will be permissible:

For hot-molded compounds	± 5%
For cold-molded compounds	±10%

All specimens shall be conditioned before testing by drying in an oven at 50° C.±5° C. for 48 hrs., followed by cooling to room temperature in a dessicator. Five specimens shall be tested at room temperature. The speed of the head of the testing machine shall be such that the load can be accurately weighed, but shall not exceed 0.050-in. (1.27 mm.) per minute with the machine running idle. All tests shall be made at normal room temperature of about 20° C. (68° F.).

The report shall include the following:

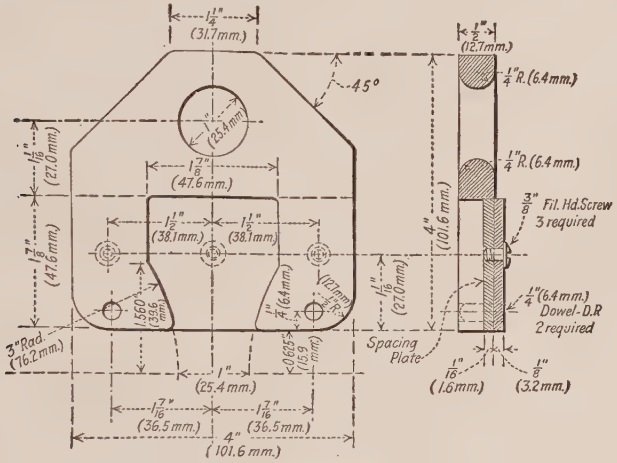
(*a*) The breaking load of each specimen in pounds or kilograms;

(*b*) The thickness and width of each specimen in inches or millimeters as measured by a micrometer at the center of the specimen, that is, the point of minimum section;

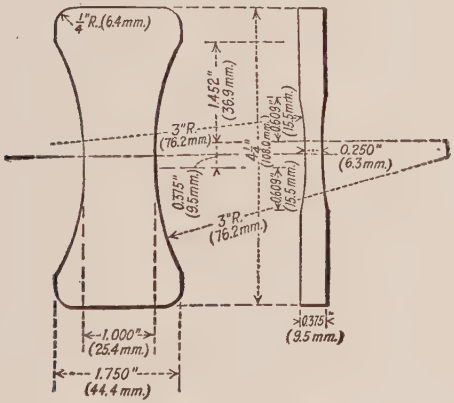
(*c*) The ultimate tensile strength in pounds per square inch or in kilograms per square millimeter of each specimen, calculated from the minimum area measured at the center of the test specimen before the load is applied;

(*d*) The character of the material tested, with description of the fracture and its location with respect to the middle point of the specimen.

(*e*) The speed in inches or millimeters per minute at which the head of the testing machine traveled during the test.



(*a*) Specimen holder.



(*b*) Tension test specimen.

FIG. 212.—Tension Test Specimen and Holder.

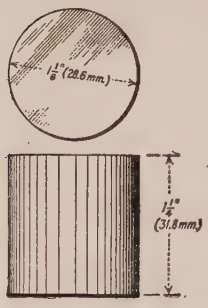
Compressive Strength

This method has similarly been standardized as follows:

Any standard testing machine may be used provided it is accurate to within 1% of the lowest load for which it is used. One end of the specimen

shall bear upon an accurately centered spherical bearing block, located whenever practicable at the top, and the metal bearing plates shall be directly in contact with the ends of the test specimen.

The test specimen shall be molded in the form of a cylinder having a height of 1.25 in. (31.8 mm.) and a diameter of 1.125 in. (28.6 mm.) (Fig. 213). The ends shall be flat and perpendicular to the axis, being ground to this condition if necessary.



Courtesy A.S.T.M.

FIG. 213.—Compression Test Specimen.

NOTE 1.—To permit the use of one mold for all molding compounds the following variations in dimensions of the test specimen will be permissible:

For hot-molded compounds	± 5%
For cold-molded compounds	±10%

NOTE 2.—Due to the size and shape of this specimen, it is sometimes difficult to completely cure it within the relatively short time which would ordinarily be used and with the temperatures ordinarily used. This is particularly true when hand molds, that is, molds heated by conduction from the platens, are used. It is, therefore, recommended that special precautions be taken to insure thoroughly cured parts, experiments indicating that 20 to 30 minutes may be necessary in some cases with hand molds.

All specimens shall be conditioned before testing by drying in an oven at 50° C.±5° C. (122° F.±9° F.) for 48 hrs., followed by cooling to room temperature in a desiccator. Five specimens shall be crushed at room temperature.

Additional tests shall be made at elevated temperatures, the actual temperatures selected depending upon the use that is to be made of the material. Five specimens shall be tested at each temperature selected. The specimen shall be kept at that temperature a sufficient length of time to become of uniform temperature throughout and shall be maintained at that temperature during the test.

The load shall be applied on the ends of the specimen and the cross-head speed of the testing machine shall be such that the load can be accurately weighed but shall not exceed 0.050 in. (1.27 mm.) per minute when the machine is running idle. For the best results use the slowest possible speed.

The report shall include the following:

(*a*) The dimensions of each specimen in inches or in millimeters;

(*b*) The load on each specimen in pounds or kilograms at the first sign of failure;

(*c*) The ultimate compressive strength in pounds per square inch or kilograms per square millimeter of each specimen, calculated from the measured area of each specimen before the load is applied;

(*d*) The general character of the material tested, with description of how it acts under the applied load;

(*e*) The speed in inches or millimeters per minute at which the head traveled during the test. The time required for testing each specimen should be recorded.

(*B*) SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

Separation of the Bituminous Matter and Discrete Aggregate

Bituminized aggregates are separated into their bituminous and discrete components for the combined purposes of ascertaining the percentage and nature of the mineral constituents and for examining the physical and chemical characteristics of the bituminous binder, with the object of its identification or duplication.

Hot Extraction Method.—This has been standardized as follows:

Bituminous grouts shall be heated in an oven or on a hot plate in a pan or other suitable container at the lowest possible temperature to prevent overheating and volatilization, and when sufficiently fluid, shall be thoroughly stirred to insure a uniform sample, whereupon 10 to 30 g. shall be taken for analysis.

Asphalt mastics or mastic cake shall be warmed on a hot plate or in a hot oven until soft enough to be broken up or stirred, so that a representative sample for analysis may be taken. The amount taken for analysis will depend upon the amount of coarse gravel or stone in the mixture. The larger the gravel or stone, the larger will be the sample required for accuracy. The size of samples to be taken shall be as follows: Where all particles pass a No. 10 sieve, 10 to 30 g.; where 25% of the aggregate is retained on a No. 10 sieve, 50 g.; where 50% of the aggregate is retained on a No. 10 sieve, 100 g ; and where 75% of the aggregate is retained on a No. 10 sieve, 200 g.

(*a*) ***For Analysis of 10- to 30-g. Samples.***—In cases where a 10- to 30-g. sample is sufficient, the analysis shall be carried out by means of the glass extractor illustrated in Fig. 207.

An ordinary fat-free Whatman or S. and S. filter thimble, 60 mm. in length by 26 mm. outside diameter, shall be dried for 30 minutes in an oven at 212° F., allowed to cool in a desiccator, and then weighed in a suitable weighing bottle. The weighed sample shall be placed in the thimble and a disc of wool felt or a plug of absorbent cotton shall be placed over the sample in the top of the thimble to distribute the solvent uniformly and prevent splashing. After placing in the extractor, 40 to 50 ml. of carbon disulfide shall be poured over the sample, whereupon the thimble containing the sample shall be suspended under the condenser by a fine wire bail. The flask shall be cautiously heated by a steam-bath or electric heater just enough to vaporize the solvent. Cold water is circulated through the condenser. The heat evaporates the carbon disulfide in the flask. This condenses upon the condenser and drops back upon the sample through which it filters, thus dissolving out the bitumen which collects in the bottom of the flask.

The extraction should be discontinued when the carbon disulfide drops colorless from the filter. The time of extraction will depend upon the nature of the bitumen and mineral aggregate in the sample and upon the degree of heat applied, the coldness of the water in the condenser and other factors. In some cases extraction may be complete in one hour, in others four or five hours may be necessary.

When the solvent comes through clear, the filter shall be removed and washed with a fine jet of carbon disulfide from a washing bottle to wash out any bitumen

that may be retained at the top of the paper and to break up any channels that may have been formed by the carbon disulfide passing through. If the washings show any color, the thimble shall be put back and extraction continued until the solvent again becomes colorless. It shall then be removed, dried carefully, at a low temperature at first to prevent ignition of the absorbed carbon disulfide, and finally to constant weight at 100° C. (212° F.), cooled and weighed.

An aliquot portion of the solution in the flask shall be rinsed into a weighed porcelain or silica evaporating dish or crucible and the solvent burned off under a hood. The residue shall be ignited over a flame or in a muffle and the ash weighed and the weight added to that of the mineral matter in the filter paper. This is to correct for the fine mineral matter which will be carried through the paper by the solvent. Should there be a considerable amount of ash recovered in this way, and if it is found that the mineral matter is calcium or other carbonate, it shall be recarbonated by repeated treatment with ammonium carbonate solution and finally ignited at a dull red heat. Ordinarily, however, the mineral matter going through the paper will be so small in amount that the difference caused by ignition may be neglected. The corrected loss in weight on the original sample represents the percentage of asphalt present.

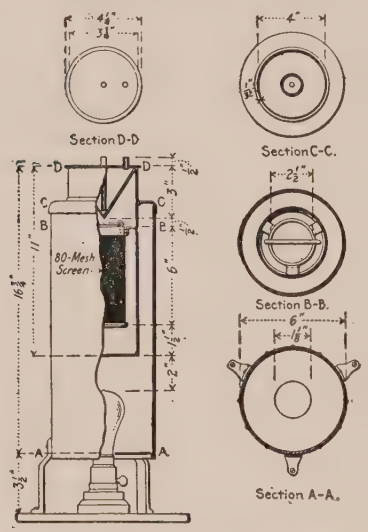


FIG. 214.—Extraction Apparatus.

(*b*) ***For Analysis of 50- to 500-g. Samples.***—The apparatus for analysis of samples containing coarse aggregate shall be the large extractor shown in Fig. 214, consisting of a large brass cylinder, through the bottom of which projects a 16-candle-power incandescent carbon filament bulb to supply heat to the extraction apparatus proper, which is held in the upper portion of the cylinder. This apparatus is composed of a cylindrical brass vessel for holding the solvent, a cylindrical wire basket made of 80-mesh wire cloth suspended in the cylinder, and an inverted conical condenser which serves as a top.

A large filter paper, 12 or 13 in. in diameter, shall be fitted inside the wire basket of the extractor by folding once more than in ordinary filtering, or by wrapping it over a form which fits inside the basket (a cylindrical bottle of proper size makes a good form) and placing it inside the basket.

The basket with contained filter paper shall be dried and weighed. The sample shall be weighed and packed in the filter paper in the basket. Care should be taken not to pack all coarse particles in one place and the fine particles in another, but to have them mixed together in uniform proportions.

The sample shall be covered with a disk of felt or wad of absorbent cotton to insure even distribution of the dropping solvent, thus preventing it from forming a channel through the sample. The basket shall be suspended in the extractor and 150 to 200 ml. of carbon disulfide poured over the felt or cotton.

The condenser shall be placed over the top and water circulated through it. Current shall be started through the electric lamp underneath the extractor and the extraction carried on exactly as in the smaller glass extractor, but on a larger scale. The time for extraction will vary from 3 to 12 or more hours, depending upon the nature of the sample.

To determine when extraction is complete, the condenser shall be raised and the basket lifted out to observe if drippings are clear. One or two drops caught upon white filter paper should leave but a light stain.

The drying and weighing of the basket, burning off of the solution for correction, and calculation of the weight of mineral matter shall be determined as in the foregoing. Note that any water in chemical combination with the mineral constituents is not ascertained by this procedure, but the amount present is usually so small as to be negligible.

Cold Extraction Method.—Weigh out 1000 g. of the well-disintegrated sample into an 800 ml. beaker and add 500 ml. carbon disulfide. Stir five or six times during the first 24 hours thoroughly to break up the aggregate, and then let stand quietly for 48 hours, after which the solution shall be carefully decanted and filtered through a series of three 100 ml. funnels, using absorbent cotton as the filtering medium. The aggregate left in the beaker shall be subjected to a second washing, conducted as described. The extracts shall be combined and placed in a quart jar, which shall be tightly covered and allowed to stand quietly for 48 to 72 hours, after which the solution shall be filtered through an asbestos mat in a Gooch crucible to remove the last traces of sediment. The mineral ingredients shall then be dried and weighed as previously described.

In the case of mastic block and similar bituminized aggregates containing a high percentage of finely-divided mineral matter, there is apt to be a loss of fine material, caused by carbon disulfide solution creeping behind the folds of the filter paper and over its edge, rather than through the paper. In the case of mastic the following procedure is recommended: Two 32-cm. No. 5 Whatman filter papers, after being dried in an oven and cooled in a desiccator, are counterpoised.

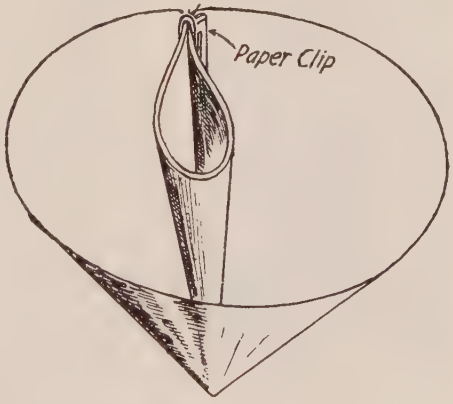


Fig. 215.—Method of Folding Filter-papers for Extraction Test.

These papers are folded together and fastened with a paper-clip in the manner shown in Fig. 215, whereupon they are placed in a glass funnel 7-in. in diameter, the top edge of which is ground flat. The funnel is covered with an 8-in. diameter glass plate, in the center of which a $\frac{5}{8}$-in. diameter hole has been drilled. To make certain that the plate completely closes the funnel, it is advisable to secure the plate to the funnel with gelatine cement, prepared by dissolving 10 g. of gelatine in 80 ml. water and adding 20 g. glycerin. The mastic block is warmed in an oven and broken into small pieces. Two 75 g.

representative samples should be taken and run in duplicate. One sample is introduced into the counterpoised filter and the funnel covered with the glass plate as described. Carbon disulfide is introduced directly into the funnel through a 1500 ml. separatory funnel as shown in Fig. 216. The addition of carbon disulfide may be made automatic, so that when the level of the liquid in the filter falls below a predetermined height, a fresh supply will be admitted, and this may continue overnight without attention. When the filtrate comes through colorless, the carbon disulfide supply is stopped and the paper allowed to dry, first in air, and finally in an oven at 120° C. for one hour. After cooling in a desiccator, the filter and contents are weighed, the outside paper being placed on the weight-pan as a counterpoise. The weight of asphalt extracted is ascertained by subtracting the weight of the aggregate from the weight of the sample taken, and its percentage calculated.

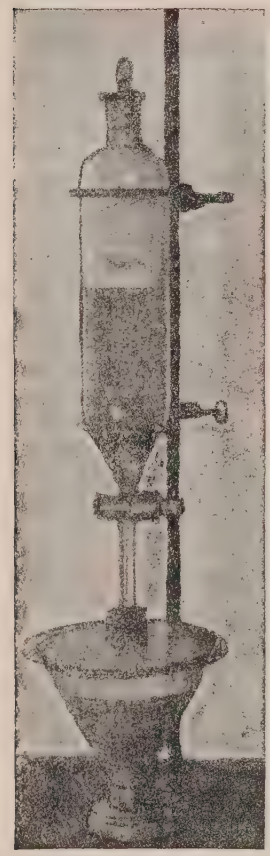


FIG. 216.—Apparatus for Cold Extraction Test.

For products other than mastics, the following weights of material are recommended: surfacings containing aggregate all passing 10-mesh: two 50 g. samples; surfacings containing up to 25% ¼-in. or ⅜-in. aggregate: two 150 g. samples; surfacings containing up to 25% ¾-in. aggregate: two 300 g. samples; surfacings containing up to 50% ¾-in. aggregate: two 500 g. samples.

Another variation consists in covering the coarsely broken sample with carbon disulfide and allowing same to stand quietly overnight, whereupon it will be found that most of the soluble material has gone into solution. The residue is then washed with 8 to 10 portions of carbon disulfide. Fine mineral matter is removed from the combined extracts by filtering or centrifuging.

Centrifugal Extraction Method.—The most efficient apparatus of this type is illustrated in Figs. 217 and 218. It consists of a 1/5 h.p. vertical motor *a*, capable of making 1100 revolutions per minute at 110 volts, with either direct or alternating current. Its shaft projects into a cylindrical copper vessel *b*, having a concave bottom and draining into the spout *c*. A circular brass plate *d*, 9½ in. in diameter supports an inverted iron bowl *e*, 8½ in. in diameter by $2\frac{5}{16}$ in. high, having a 2-in. circular hole at the top. A brass cup *f* is fastened to the inner side of the bowl, having a circle of ⅛ in. holes for the admission of solvent, and terminating in a hollow axle which fits snugly through a hole in the center of the brass plate *d*. A felt ring *g*, ¾ in. wide and about 0.090 in. thick (cut from No. 80 roofing felt) is firmly pressed against the bowl by the milled nut *h* for which the hollow axle is suitably threaded. The axle in turn fits snugly over the shaft of the motor, to which it is secured by a slot and cross-pin.

Procedure.—The filter ring shall be dried for 30 minutes in an oven at 212° F., allowed to cool in a desiccator and then weighed.

The required quantity (10 or 25 g.) of the disintegrated sample shall be accurately weighed on a tared watch glass or weighing scoop. The sample shall then be placed in the bowl of the rotarex machine, care being taken to evenly distribute the mixture around the periphery of the bowl to prevent vibration during the extraction. The filter ring and bowl plate shall then be placed on

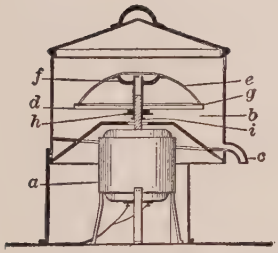


FIG. 217.—Centrifugal Extractor.

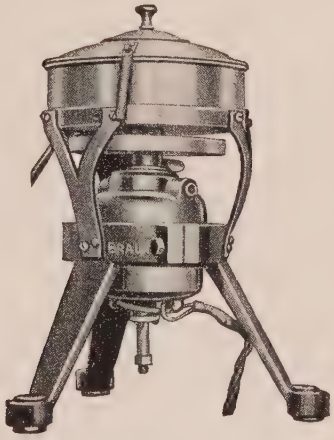


FIG. 218.—Centrifugal Extractor.

the bowl and fastened down fairly tight. The bowl shall then be placed in position in the rotarex machine and from 40 to 50 ml. of carbon disulfide poured into the bowl through the funnel opening. After allowing the material to digest for about 15 minutes, the motor shall be started, slowly at first, and then the speed increased sufficiently to cause the dissolved bitumen to flow from the spout in a thin stream. The dissolved bitumen or filtrate shall be collected in a beaker or other receptacle. When the first charge has drained, the motor shall be stopped and a fresh charge of carbon disulfide added and again allowed to digest for 15 minutes and the machine started as before. This operation shall be repeated from three to five times or until the solvent runs clear from the spout showing all bitumen has been dissolved from the sample, this usually requiring three to four washings.

When the last addition of solvent has drained off, the bowl shall be removed and placed with the bowl plate and filter ring on a sheet of glazed manila paper and allowed to dry at room temperature. The aggregate shall then be brushed from the bowl onto the paper together with any aggregate adhering to the bowl plate and filter ring. The aggregate shall then be transferred to a tared watch glass or pan and together with the filter ring dried in an oven at 212° F., cooled in a desiccator and weighed.

In making the correction for the mineral matter suspended in the filtrate, add sufficient carbon disulfide to bring the same to a definite volume and a multiple of 100 ml. The whole filtrate shall then be thoroughly shaken so that the mineral matter is uniformly dispersed throughout the filtrate and an aliquot

part of 100 ml. then taken and transferred into a weighed porcelain or silica evaporating dish and the solvent burned off under a hood. The residue shall then be ignited over a gas flame or in a muffle until it is entirely free from carbon, cooled and weighed and the total ash correction determined as follows:

$$\text{Total ash} = \frac{\text{Total filtrate in ml.} \times \text{Ash in grams recovered in aliquot part}}{\text{Aliquot part in ml.}}$$

Should there be a considerable amount of ash recovered in this manner, and if it is found that the mineral matter is calcium or other carbonate, it should be recarbonated by repeated treatment with ammonium carbonate solution and finally ignited at a dull red heat.

An alternate procedure consists in using a centrifugal tube in the following manner: The apparatus to be used in this test shall be any suitable type of centrifugal machine capable of being rotated rapidly (1800 r.p.m.) surmounted by a head carrying an equal number of metal tube shields, slightly larger than the glass tubes used, and provided with rubber cushions, the whole being encased in a metal shield. In place of glass tubes aluminum or bronze tubes may be used.

Procedure.—The required quantity (10 or 25 g.) of the disintegrated sample selected at random throughout the sample shall be accurately weighed on a tared watch glass or weighing scoop. After weighing, the sample shall be transferred to a numbered and weighed tube. The tube shall be filled with a definite quantity of carbon disulfide approximately three-fourths full and then inserted in the metal tube shield of the centrifuge machine. The tubes shall be so placed in the centrifuge machine as to have equal weights opposite each other around the head of the centrifuge. After allowing the material in the tube to digest for about 15 minutes, the centrifuge machine shall be started, slowly at first, gradually bringing it up to full speed and whirling from 5 to 10 minutes. The machine shall then be stopped, the tube removed and the solvent and dissolved bitumen decanted into a numbered flask. The tube shall again be filled with carbon disulfide, mixing the solid matter at the bottom of the tube with the solvent by stirring, the material allowed to digest for 15 minutes, whirled from 5 to 10 minutes, the solvent decanted and the bitumen dissolved as before. This operation shall be repeated from three to five times or until the solvent in the tube, after whirling from 5 to 10 minutes, is clear and colorless.

The tube shall now be removed from the machine and the solvent allowed to evaporate from the aggregate at room temperature and the material then dried in an oven at 212° F. to constant weight, cooled in a desiccator and weighed.

The solvent and dissolved bitumen in the flask shall be rinsed into a weighed porcelain or silica evaporating dish and the solvent burned off under a hood. The residue shall then be ignited over a gas flame or in a muffle until it is entirely free from carbon, allowed to cool in a desiccator and the ash weighed and its weight added to the weight of the mineral matter in the tube. Should there be a considerable amount of ash recovered in this manner, and if it is found that the mineral matter is calcium or other carbonate, it shall be recarbonated by repeated treatment with ammonium carbonate solution and finally ignited at a dull red heat. Ordinarily the mineral matter in the solution is found to be so small that the difference caused by ignition may be neglected.

PART III

EXAMINATION OF BITUMINIZED FABRICS

This caption includes the following groups of products, viz.:

Q—Prepared roofings.
R—Composition shingles.
S—Deck and porch coverings.
T—Bituminized fabrics for constructing built-up roofs.
U—Bituminized fabrics for constructing waterproofing membranes.
V—Electrical insulating tape.
W—Waterproof papers for wrapping and packing.
X—Waterproof papers for insulating against heat or cold.
Y—Felt-base floor coverings (surfaced with linseed oil and pigment composition).
Z—Expansion joints for pavements.

These are constructed as shown in Table III, where the index *a* indicates that asphaltic compositions have been used, and *t* signifies that coal tar (pitch) *et al.*, have been used.

TABLE III

	Paper		Burlap		Duck		Light Cotton Fabric		Rag-Felt		Asbestos Felt		Burlap and Rag or Asbestos Felt		Paper and Light Cotton Fabric	
	a	*t*	*a*	*t*	*a*	*t*	*a*	*t*	*a*	*t*	*a*	*t*	*a*	*t*	*a*	*t*
Single Layered:																
Saturated only	**WX**	WX	U	U	...	...	...	...	**TUY**	**TU**	T	...	....	...	...	...
Coated only (one or two sides)	W	....	**U**	**U**	**S**	...	...	...	.....	....	....	...	....	...	...	...
Saturated and coated	**X**	....	U	U	QS	...	**V**	...	**QR**	....	Q	...	....	...	...	...
Laminated (Bituminated):																
Layers saturated only	....	....	Z	...	...	...	...	...	**Z**	Q	QT	...	UZ	U	...	...
Layers saturated and coated	....	....	...	...	...	...	...	...	Q	....	Q	...	Q	...	...	...
Layers unsaturated	**W**	W	...	...	...	...	...	...	.....	....	....	...	....	...	W	W
One layer unsaturated and others saturated	**W**	W	...	...	...	...	...	...	.....	....	....	...	....	...	W	W

NOTE.—Letters in heavy type indicate the more important groups of products.

The finished products falling in this class include sheet roofings, floor coverings, waterproof membranes, sheathing and insulating papers, expansion joints involving the use of woven or felted fabrics, electrical insulating tape, and certain types of wall board. As these are constructed in many different ways, it will obviously be impracticable to describe in detail the analytical methods applicable to each. The ones which follow have been devised specifically for examining prepared roofings, but with these as a starting-point, others may readily be evolved for testing floor coverings, waterproof membranes, sheathing and insulating papers, etc.

(*A*) PHYSICAL TESTS OF THE FINISHED PRODUCT

Weight per Unit Area

(*a*) ***For Saturated Felted and Woven Fabrics.***—The width of each roll taken shall be measured to the nearest $\frac{1}{32}$ in. The minimum and maximum width so obtained shall be reported.

Each roll taken shall be weighed intact to the nearest ¼ lb. and the minimum and maximum gross weight shall be reported.

Each roll sampled shall be stripped. All the wrappers and packing material shall be weighed together to the nearest ¼ lb. and the average weight thereof per roll shall be reported. Each roll shall then be unwound, observing the workmanship and finish while so doing. The length and width of each roll shall thereupon be measured to the nearest ¼ in. and the square feet of material contained in each roll calculated.

The rolls shall be rewound, fastened with pieces of light string and then each roll shall be weighed to the nearest ¼ lb. In the case of felted fabrics, calculate the weight of each roll in pounds per 100 sq. ft. and report the maximum and minimum, likewise recording the average for the rolls sampled, which shall be regarded as the corresponding weights of the entire shipment. In the case of woven fabrics, calculate the weight of each roll in ounces per square yard, and report the minimum, likewise recording the average for the rolls sampled, which shall be regarded as the corresponding weights of the entire shipment.

From the rolls examined, select the one whose weight per unit area is nearest the average weight per unit area of the lot. The roll so selected shall be laid flat, the first convolution or two carefully unwound, and with a knife and straight edge the sheet shall be cleanly cut across at right angles to the edges. A section measuring 30 in. in the direction of the roll's length shall be removed. If the material is surfaced with sand or other fine material, any detached particles belonging to each 30-in. section shall be retained. The width of each section shall be measured to the nearest $\frac{1}{32}$ in. Each section, together with any detached surfacing, shall be weighed to the nearest gram. The weight in pounds per 100 sq. ft. or the weight in ounces per sq. yd. shall be calculated from the formulas:

$$\text{Pounds per 100 sq. ft.} = 1.0582 \times \frac{\text{Weight of 30-in. section in grams}}{\text{Width of 30-in. section in inches}}$$

$$\text{Ounces per sq. yd.} = 1.5238 \times \frac{\text{Weight of 30-in. section in grams}}{\text{Width of 30-in. section in inches}}$$

This must check within 1% of the average weight per unit area of shipment. If the sample fails to do this, then additional samples shall be cut from the same roll, until one is obtained which does, which sample shall be kept for further examination.

NOTE.—As a referee method or in case any dispute arises regarding the properties as may be ascertained from the particular sample selected, a 30-in. sample shall be taken and examined separately from each roll sampled as above.

If the material is surfaced with sand or other finely comminuted material, the surfacing shall be swept with a moderately stiff brush from all the 30-in. sections taken. All the material thus removed shall be caught and weighed to the nearest ounce. From the aggregate areas of all the sections taken, the average weight of detached comminuted surfacing shall be calculated in pounds per 100 sq. ft.

The 30-in. section selected for examination shall be cut into sections for further tests in the manner shown in Fig. 219.

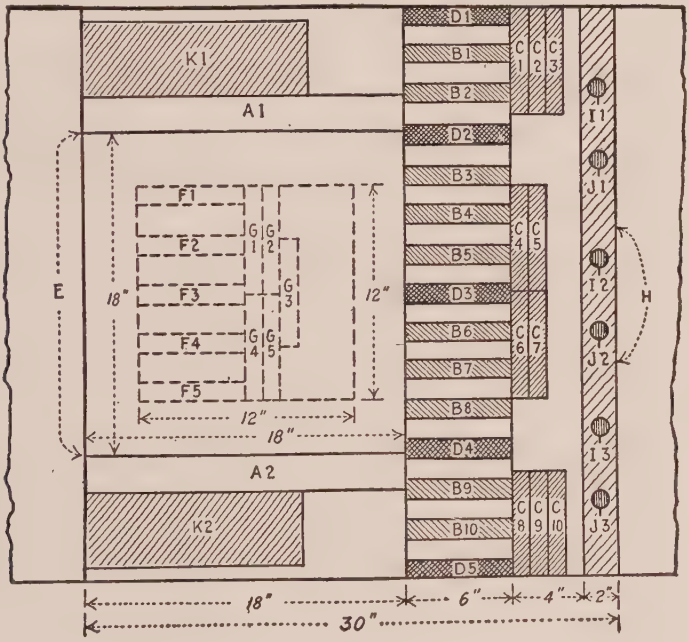


FIG. 219.—Sampling Bituminized Fabrics.

(*b*) ***For Smooth-roll and Mineral-Surfaced Roll-Roofing.***—Each roll selected shall be weighed to the nearest ¼ lb. The wrappers, packing material, nails, and cement from each roll shall be weighed together to the nearest ¼ lb. and the average weight thereof per "square" shall be recorded. The quantity and character of nails and cement shall be recorded.

Each roll shall be unwound and the workmanship and finish of the roofing observed. Record the weight of any loose surfacing that may fall off in so doing.

The length and width of each roll shall be measured to the nearest ¼-in., and the square feet of material contained in each roll shall be calculated. From these values, the average area of the rolls examined shall be calculated.

From the above net weight, exclusive of loose surfacing, of roofing per 108 sq. ft. contained in each roll shall be calculated and the minimum weight per 108 sq. ft. of the lot.

The average weight per 108 sq. ft. for the rolls examined shall be calculated. This shall be regarded as the average weight per 108 sq. ft. of the lot. . . . (1*a*)

From the rolls examined, the one whose weight per 108 sq. ft. is nearest the average weight of the lot shall be selected. The first convolution or two shall be unrolled, and with a knife and straight edge, the sheet shall be cut across at right angles to the edges. A section measuring exactly 30 in. in the direction of the roll's length shall then be removed. The width of this section shall be measured to the nearest $\frac{1}{32}$ in. and weighed, neglecting any loose surfacing. The weight in pounds per 108 sq. ft. shall then be calculated from the following formula:

$$\text{Pounds per 108 sq. ft.} = \frac{\text{Weight of 30-in. section in ounces}}{\text{Width of 30-in. section in inches}} \times 32.4 \qquad (1b)$$

The weight so determined shall check within 1.5% of the average weight per 108 sq. ft. of the lot (1*a*). If this sample fails to check, then additional samples shall be cut from the same roll, until one is obtained which does, which sample shall be kept for further examination.

NOTE.—As a referee method, or in case any dispute arises regarding the properties as may be ascertained from the particular sample selected, a 30-in. sample shall be taken and examined separately from each roll sampled.

(*c*) ***For Mineral-surfaced Shingles.***—Each bundle selected shall be weighed to the nearest ¼ lb. The packing material shall be weighed to the nearest ¼ lb. and the weight recorded separately for each bundle. The average weight of packing material per "square" shall be recorded.

The shingles in each bundle, "*a*," shall be counted and the workmanship and finish of the shingles shall be observed. Record the weight of any loose surfacing that may fall off in so doing.

From the above the net weight of each bundle, exclusive of loose surfacing, shall be calculated, "*b*," The dimensions of two representative shingles shall be accurately measured and the net area of material in each shingle calculated in square feet, "*c*."

The area in square feet of material contained in each bundle ($a \times c$) shall be calculated. The weight of roofing material per 108 sq. ft. contained in each bundle $\left(\frac{b}{a \times c} \times 108\right)$ shall be calculated, and the minimum weight per 108 sq. ft. recorded. This shall be regarded as the minimum weight per 108 sq. ft. of the lot.

The average weight (*d*) per 108 sq. ft. for the bundles examined shall be calculated. This shall be regarded as the average weight per 108 sq. ft. of the entire shipment . . . . . (1*a*)

The average weight per shingle $\left(\frac{c \times d}{108}\right)$ shall be calculated..... (1*b*)

From the bundles selected, a definite number of representative shingles, whose weight shall fall within 1.5% of the average weight ascertained in (1*a*) shall be taken for further examination. The number of shingles so selected shall represent as closely as possible 6 sq. ft. of material, and shall be selected as far as possible from different bundles.

NOTE.—As a referee method, or in case any dispute arises regarding the properties as may be ascertained from the particular sample selected, then a similar sample shall be taken and examined separately from each bundle of shingles sampled.

Thickness

The thickness of each specimen shall be measured at 10 equally spaced points, 1 in. from a cut edge, with a micrometer gage having flat bearing surfaces at both contact points of not less than ½ in. in diameter and preferably of the spring-and-dial type. The readings for each roll sampled shall be averaged and the minimum, maximum and average thickness calculated to the nearest 0.001 in.

Resistance to Heat

(*a*) ***For Asphalt-saturated Fabrics.***—From each specimen, 12 by 6-in. strips shall be cut at *K*-1 and *K*-2 in Fig. 219., care being taken not to disturb any of the detached surfacing. Each strip shall be weighed and suspended in the center of an air-oven maintained at 221° F. (105° C.)±5° F. (3° C.) with a thin wire fastened through holes punctured near one edge. The thermometer shall be inserted in the oven to such a depth that its bulb will be in line with the center of the specimens. The strips shall be kept in the oven for exactly five hours, then cooled and removed carefully, and each specimen weighed. The average loss shall be calculated as a percentage and the average percentage of moisture deducted. The final figure shall represent the average loss on heating, exclusive of moisture.

(*b*) ***For Coal-tar Saturated Felt Only.***—From the rolls making up the sample, strips 6 in. wide shall be cut across the sheet. Sufficient of these shall be taken to make up a sample of 250 g.±5.0 g. These strips then shall be rolled up and placed in the wire basket of the extraction apparatus described on p. 1568. The sample shall then be covered with a disk of soft filter paper to insure an even distribution of the solvent.

The carbon disulfide extract containing the bitumen shall be transferred to a 500-ml., short-neck, round-bottom flask. The flask shall be equipped with a Hempel column, 16 cm. in length, 15 mm. in inside diameter and filled to a depth of 5 cm. with glass beads. The Hempel column shall be connected with a water-cooled condenser. A −2 to +80° C. thermometer shall be placed in the Hempel column so that the top of the bulb shall be opposite the bottom of the tubulature. Distillation for the removal of carbon disulfide shall be continued by means of a steam bath until drops cease to fall from the condenser. The distillation then shall be carried out over a small flame, heating carefully and observing the thermometer until the distillation ceases and the temperature of the vapor as indicated by the thermometer shows no further rise on slightly increasing the flame.

When the contents of the flask are sufficiently cool to be poured without appreciable vaporizing, 100 g. ±0.1 g. shall be distilled as on p. 1533.

Fractions shall be taken at 210° C. and 235° C. and the distillation stopped at that point. The per cent of distillate by weight at each temperature shall be calculated on the basis of the weight of sample taken for distillation.

(*c*) ***For Asphalt Roll-roofings and Shingles.***—Two strips shall be cut from the sample of roofing or shingles, each approximately 8 by 8 in. They shall be weighed and suspended vertically in the same direction as the material would be applied to the roof, in the center of an air-oven maintained at 176° F. (80° C.) ±5° F. (3° C.) with a thin wire fastened through holes punctured near one edge. The internal dimensions of the oven shall not be less than 12 by 12 by 12 in. An electrically heated oven is recommended. The thermometer shall be inserted in the oven to such a depth that its bulb will be in line with the center of the specimens. The strips shall be maintained at the prescribed temperature for exactly two hours, then cooled in a desiccator and each specimen weighed. The average loss shall be calculated as a percentage. Any change in appearance of the specimen shall be recorded, such as flowing, sagging, blistering or absorption of the coatings; also sliding of granular surfacing.

(*B*) SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

Separation of Bituminous Matter, Mineral Matter and Fibrous Constituents

Moisture

From each specimen, 2-in. strips shall be cut, as shown at *A*-1 and *A*-2 in Fig. 219. The 2-in. strips shall be cut into 1-in. squares. About 50 g., selected at random, shall be accurately weighed and distilled with 100 ml. of a coal-tar distillate of which 5 to 10% boils below 100° C. (212° F.) and of which at least 90% distills up to 180° C. (356° F.), in an apparatus of the form and under the conditions prescribed on p. 1553. The flask containing the solvent and sample shall be heated in a paraffin bath at a temperature of 302 to 338° F. (150 to 170° C.) until no further water passes over. The distillate shall be allowed to stand in the graduated receiver until the water separates, whereupon the volume of water shall be measured and its weight calculated. From this, the average percentage of moisture in the fabric, as received, shall be calculated.

Analysis of Saturated Fabrics

From each roll sampled, a 2-in. strip (within $\frac{1}{32}$ in.) shall be cut across the specimen, as shown at *H* in Fig. 219.

Each strip shall be extracted with carbon disulfide in an extractor shown in Fig. 219, the extraction being continued for several hours after the drippings have become colorless. The desaturated fabric shall be removed and heated in a ventilated oven at 225° F. (107.1° C.), cooled in a desiccator, any adhering comminuted surfacing being brushed off and retained, and weighed as rapidly as possible. The heating shall be repeated until the weight of the fabric re-

mains constant, as determined by two consecutive weighings taken not less than ten minutes apart, which shall show a further loss of not more than 0.1%. This will give the weight of the fabric in the moisture-free state. Where a coal-tar pitch saturant has been used, the moisture-free weight of the desaturated fabric shall be corrected for the carbonaceous matter retained mechanically in its interstices, by means of the method described in the following paragraph.

The following colorimetric method shall be used to ascertain the carbonaceous matter derived from a coal-tar pitch saturant and retained by the desaturated fabric:

(*a*) About 15 g. of an unsaturated fabric of the same general character as the one under examination, shall be macerated by boiling in water, disintegrating with a rotary egg-beater and picking the fibres apart with needles. The fibres shall be filtered through fine cloth and dried at a temperature of 225° F. (107.1° C.) to constant weight. One gram of the fibres shall be accurately weighed into a flask and diluted to exactly 100 ml. with distilled water at room temperature. About 50 g. of glass beads shall be added and the contents of the flask shaken vigorously until the fibres are reduced to a homogeneous pulp in uniform suspension.

(*b*) A distilled coal tar, having approximately 10 to 25% of insoluble carbonaceous matter, shall be procured and the carbonaceous matter extracted with benzol until it is free from soluble matter; then dried at a temperature of 225° F. (107.1° C.) to constant weight. One gram of the purified carbonaceous matter shall be accurately weighed and diluted to exactly 100 ml. at room temperature with a starch solution of a consistency sufficient to carry the carbonaceous matter into temporary suspension. (A 12.5% solution is recommended.)

(*c*) The liquid carrying the fibres, obtained as described in Paragraph (*a*), shall be titrated with the suspension of carbonaceous matter, obtained as described in Paragraph (*b*), and from time to time a field prepared from a drop of the well agitated mixture shall be examined under a microscope at 100 diameters magnification until the color exactly matches a field prepared from the desaturated fabric under examination, when both are reviewed side by side under parallel conditions. The end-point is fairly sharply defined. The burette reading gives directly the percentage of carbonaceous matter adhering to the moisture-free fabric under examination.

(*d*) The weight of moisture-free fabric shall be corrected by deducting the weight of adhering carbonaceous matter.

The total comminuted surfacing plus any filler present in the bituminous saturant represents the sum of the detached comminuted surfacing, the amount brushed off from the surface of the desaturated fabric, plus the amount recovered upon evaporating and igniting the bituminous extract obtained as above.

The weight of bituminous saturant represents the difference between the weight of the original fabric, and the sum of the weights of the moisture-free desaturated fabric, plus moisture, plus the total comminuted surfacing and filler present.

Ash.—A representative sample shall be secured by cutting from each strip of desaturated felt a piece about ½ in. in diameter as shown at *I-1*, *I-2*, and *I-3* (Fig. 219). About 25 g. selected at random from all the specimens sampled in

this manner shall be accurately weighed, and incinerated in a weighed porcelain or quartz crucible either over an open flame or in a muffle, until all the carbon is consumed. A few drops of ammonium carbonate solution shall be added, the sample ignited gently, and weighed. The percentage of ash shall be calculated on the basis of the moisture-free felt.

NOTE.—As a referee method, or in case greater accuracy is desired, the three portions taken from each specimen roll shall be weighed and ignited separately. The minimum, maximum and average of ash present shall be calculated on the basis of the moisture-free felt.

Analysis of Saturated and Coated Fabrics

Since the fabrics and bituminous matter may be assembled in many different ways, the resultant products are too numerous to itemize. It is impractical, therefore, to give analytical methods applicable to each. The ones which follow have been devised specifically for examining prepared roofings and composition shingles composed of roofing-felt, saturated and coated on both sides with asphalt, and surfaced on the top with either powdered or granular mineral matter, and on the under side with powdered mineral matter. These methods are typical ones, and with slight modifications and a little ingenuity may be adapted to other forms of bituminized fabrics.

Asphalt roll-roofings and shingles may be divided into two general types as shown in Fig. 220.

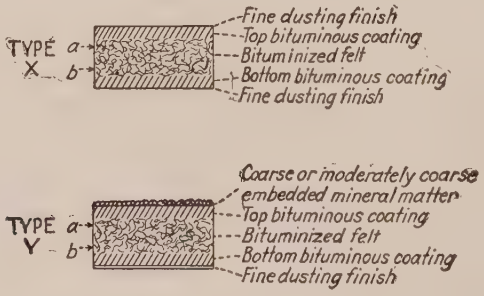


FIG. 220.—Types of Asphalt Roll-roofings and Shingles.

Type X represents a layer of felt, saturated and coated with bituminous matter, having the surface coatings dusted with fine mineral matter (e.g., talc). This type embraces what is commercially known as "smooth-surfaced roll-roofing."

Type Y is similar to Type X, but with a top surfacing of either: (1) coarse mineral matter (e.g., granular slate) embracing what is commercially known as "mineral-surfaced roll-roofing" and "mineral-surfaced shingles"; or (2) moderately coarse mineral matter (e.g., granular talc) embracing what is commercially known as "roll-roofing surfaced with granular talc."

The mineral matter, bituminous matter and fibrous matter may be distributed in the following manner:

A—Mineral Matter

1. Detached ..... } *Fine Mineral Matter* (e.g., finely ground talc or mica), Type X (on top and bottom), also Type Y (on bottom only).
2. Embedded in the top coating ..... } *Moderately Coarse Mineral Matter* (e.g., coarsely ground talc) Type Y (on top only).
3. Embedded in the bottom coating } *Coarse Mineral Matter* (e.g., crushed slate, crushed brick or tile), Type Y (on top only).
4. Admixed with the top coating (Types X and Y) ..... } May or may not be present. If present, consists of very fine mineral matter (e.g., clay, silica, limestone, slate flour, shale, etc.).
5. Admixed with the bottom coating (Types X and Y) .....
6. Ash present in desaturated felt (i.e., ash on incineration).

B—Bituminous Matter

1. Contained in the top coating.
2. Contained in the bottom coating.
3. Saturant of the felt.

C—Fibrous Matter

1. The desaturated felt.

The test strips for the separation of prepared roofing and shingles into their component parts shall be prepared as follows:

From the samples representing the average weight a number of strips shall be cut, each measuring approximately 2-in. in width by 8 in. in length. These shall be weighed, the length and width measured to within 1 mm. or $\frac{1}{32}$ in., and the weight calculated per 108 sq. ft. Any of the 2 by 8-in. strips whose weight varies more than 1.5% from the average weight of the shipment, shall be rejected, and the remaining strips shall be retained for further examination.

Note.—If a strip is cut to exactly 2 by 7.46 in. its weight in grams divided by two gives directly the weight in pounds per 108 sq. ft.

Detached Mineral Matter (*A*–1).—Remove the detached mineral particles from both sides of the 2-in. strips with a jet of compressed air operating under a nozzle pressure of 25 lb. per sq. in. and reweigh in grams. Make a correction to include any loose mineral matter. Calculate the weight in pounds per 108 sq. ft. of the detached mineral matter (*A*-1) ..... (2)

Moisture-free Felt (*C*–1).—Eight of the 2 in. by 8-in. strips shall be extracted with benzol (boiling-point 80 to 82° C.), or C.P. carbon disulfide in a suitable extractor or centrifuge, and the extraction continued until the drippings have become colorless. The desaturated felt shall be removed from the extractor, being careful not to lose any adhering mineral matter, placed in a tared weighing bottle provided with a ground-glass stopper, heated in a ventilated oven at 225° F. (107° C.)±5° F. (3° C.) for thirty minutes, the stopper inserted, then cooled and weighed. The heating shall be repeated until the weight of the felt remains constant, as determined by two consecutive weighings taken not less than ten minutes apart, which shall show a further loss of not more than 0.1%. Any adhering mineral matter shall be brushed off the felt, weighed and retained for further examination. The weight of said adhering mineral matter shall be deducted to obtain the weight of the moisture-free felt. The extract and accompanying mineral matter shall be retained for further

examination. From the weights so obtained and the respective areas of the strips of desaturated felt, the weight of moisture-free felt shall be computed in pounds per 108 sq. ft., from the following formulas and the results averaged: (3)

$$\text{Pounds per 108 sq. ft.} = \frac{\text{Weight of moisture-free felt in grams}}{\text{Area of the strips in square centimeters}} \times 221.2$$

or

$$\text{Pounds per 108 sq. ft.} = \frac{\text{Weight of moisture-free felt in grams}}{\text{Area of the strips in square inches}} \times 34.3$$

The extracted felt shall be retained for examination as to weight, thickness, strength, etc.

Ash in Moisture-free Felt (*A*–6).—The strips of desaturated felt obtained as described shall be cut into squares about 2 cm. on each side and thoroughly mixed. Pieces amounting to about 10 g. shall be selected at random and dried at 225° F. (107° C.) for thirty minutes. They shall be cooled in a desiccator, accurately weighed and then incinerated in a weighed crucible either over an open flame or in a muffle until all the carbon has been consumed. A few drops of ammonium carbonate solution shall be added, the sample ignited gently, cooled and reweighed. The percentage of ash shall be calculated on the basis of the moisture-free felt..... (4)

Bituminous Saturation (*B*–3) **in Moisture-free Felt.**—From the 2 by 8-in. strips, cut 40 strips about ¾ by 2 in. and weigh, this being a convenient size to handle. These strips shall then be separated into three horizontal sections. The small arrows *a* and *b*, to the left of the various types of roofing illustrated in Fig. 220., indicate approximately where the layers should be separated. The top bituminous coating, with the embedded mineral matter, shall be removed first.

NOTE.—The purpose shall be to remove the entire coatings with some of the saturated felt adhering and no coatings left on the central section of saturated felt. The operator may accomplish this in any way that is most convenient. Care shall be taken to preserve the mineral surfacing with the layers to which it belongs if it becomes detached during the operation. A convenient manner to effect the separation consists in warming the strips in an air-oven at a temperature of approximately 176° F. (80° C.); then with a knife, the front and back coatings, respectively, shall be peeled off, care being taken to remove as little as possible of the saturated felt, and at the same time to make sure that all of the coatings and surfacings are stripped from the felt.

These three horizontal sections thus obtained shall be weighed separately and the total weight should agree within 1% with the original weight of the strips which have been separated. The saturated felt (middle section) shall be extracted with benzol (boiling point 80° to 82° C.) or c.p. carbon disulfide, in a suitable extractor or centrifuge and the extraction continued until the washings have become colorless. The desaturated felt shall be removed from the extractor, placed in a tared weighing bottle provided with a ground-glass stopper, heated in a ventilated oven at 225° F.±5° F. (107° C.±3° C.) for 30 minutes, the stopper inserted, then cooled and weighed. The heating shall be repeated until the weight of the felt remains constant as determined by two consecutive weighings taken with an intervening heating period of not less than 10 minutes, which shall show a further loss in weight of not more than 0.1%. Calculate the weight of bituminous saturation by difference. The

saturant may be recovered by combining the extract and washings in a 200-ml. distilling flask, provided with a dropping funnel to add the solution during distillation, to which is attached a water-cooled condenser and a receiver, the latter having a vented connection to a vacuum pump. The distilling bulb is immersed in a bath having a temperature of about 212° F. (100° C.) if the solvent were carbon disulfide and a temperature of about 275° F. (135° C.) if benzol or chloroform were used as the solvent. Distillation shall be continued at this temperature at atmospheric pressure until no more solvent is evolved, after which vacuum shall be applied very gradually until a vacuum of 0.5 in. mercury pressure is attained. Great care shall be exercised in applying the vacuum gradually to prevent foaming. This vacuum shall be continued for one hour after the specified vacuum has been reached. The distilling flask shall then be disconnected and the residue represents the felt saturant and shall be weighed.

NOTE.—Use the residue of bituminous saturation recovered from the felt for examining its physical and chemical characteristics.

Calculate the per cent of bituminous saturation (*B*-3) carried by the dry felt..... (5)

Calculate the weight in pounds per 108 sq. ft. of bituminous saturation (*B*-3) present in the dry felt, i.e. (5)×(3)..... (6)

Bituminous Matter in the Top and Bottom Coatings Respectively (*B*–1 **and** *B*-2).—Take six of the 2 in. by 8 in. strips, from which the detached mineral matter has been removed, and split them lengthwise by tearing the felt midway between the points *a* and *b*. Weigh and extract the top and bottom sections, respectively, in a suitable extractor or centrifuge. Desiccate and weigh the dry felt in each section. Separate the total embedded and admixed mineral matter recovered from each section, dry at 225° F. (170° C.), cool in a desiccator and weigh. Calculate the weight of bituminous saturant present, i.e., weight of felt recovered on extraction×(5). From the original weight of the top and bottom sections, respectively, subtract the combined weights of dry felt, bituminous saturant, embedded and admixed mineral matter. The difference represents the weight of bituminous matter in the surface-coating carried by that particular section.

Calculate the weight in pounds per 108 sq. ft. of bituminous matter (*B*-1) in the top coating..... (7*a*)

Calculate the weight in pounds per 108 sq. ft. of bituminous matter (*B*-2) in the bottom coating..... (7*b*)

Calculate the weight in pounds per 108 sq. ft. of total mineral matter embedded and admixed with the top coating..... (8*a*)

Calculate the weight in pounds per 108 sq. ft. of total mineral matter embedded and admixed with the bottom coating..... (8*b*)

To separate the bituminous constituents in the coatings for further examination and also to check the percentage of mineral matter, both detached and embedded in the top and bottom coatings, with that determined above, the detached mineral matter shall be brushed off from six weighed 2 by 8 in. strips. The strips shall again be weighed and the percentage calculated based on the original weight of strips. The outer portion of the top and bottom surface coatings, respectively, shall then be scraped off after the strips have been heated

in an oven at 212° F. (100° C.) for 30 minutes. The coatings shall be scraped off by holding a dull knife at right angles to the strip of roofing supported on a firm level surface and drawing the blade sideways under moderate pressure. Care shall be taken to avoid scraping entirely through the surface coating. This is important. The scrapings shall then be weighed and dissolved in benzol (boiling point 80 to 82° C.) or c.p. carbon disulfide; and the mineral matter separated by filtering or centrifuging and washing with successive portions of solvent. The mineral matter shall then be dried at 225° F. (107° C.), cooled in a desiccator and weighed. Calculate the percentage of mineral matter based on the original weight of roofing strips taken, which should check with that obtained previously. The bituminous matter in the scrapings shall be calculated by difference and reduced to a percentage basis on the original roofing strips used. The bituminous coating shall be recovered by evaporating off the solvent as described. Both surface coatings should be treated separately in this manner.

NOTE.—Use the separated bituminous coatings for examining their physical and chemical characteristics.

Coarse or Moderately Coarse Embedded Mineral Matter (*A*–2), **also Fine Admixed Mineral Matter** (*A*–4) **on the Top Coating of Type Y.**—The mineral matter recovered from the top sections of Type Y shall be boiled with 100 ml. water and washed through a 65-mesh copper wire screen with sufficient water to remove the fine mineral matter. The total aqueous suspension of mineral matter which passes through the screen shall then be recovered by filtering the washings through a weighed Gooch crucible, then dried at 225° F. (107° C.) and reweighed. This represents the fine mineral matter admixed with the top coating. The mineral constituents retained on the 65-mesh screen represent the coarse or moderately coarse mineral matter embedded in the top coating. This shall likewise be dried and weighed.

Calculate the weight in pounds per 108 sq. ft. of coarse or moderately coarse mineral matter (*A*-2) embedded in the top coating of Type Y..... (9)

Calculate the weight in pounds per 108 sq. ft. of fine mineral matter (*A*-4) admixed with the top coating of Type Y (*)..... (10)

Fine Embedded and Admixed Mineral Matter (*A*–2 **and** *A*–4) **in the Top Coating of Type X; Likewise Fine Embedded and Admixed Mineral Matter** (*A*–3 **and** *A*–4) **in the Bottom Coating of Types X and Y.**—Take five of the 2-in. by 8-in. strips, from which the detached mineral matter has been washed off with water, and scrape off the *outer* layer of the top and bottom coatings, respectively, by means of moderately rough sandpaper or a knife blade. Enough of the surface shall be scraped to remove every vestige of the fine embedded mineral matter, and at the same time care should be taken not to cut completely through the surface coatings into the saturated felt underneath. Then scrape off about 5.0 g. of the top and bottom surface coatings, respectively, with a sharp knife as described, taking care not to scrape entirely through the surface coatings. Ignite the 5.0-g. portions separately in a tared crucible until all the carbon has been consumed, add a few drops of ammonium carbonate solution, ignite to a dull red heat and weigh.

* Up to 2% admixed mineral matter probably adventitious and not filler.

Calculate the *percentage* by weight of fine mineral matter admixed with the top coating (Type X)..... (11*a*)

Calculate the *percentage* by weight of fine mineral matter admixed with the bottom coating (Types X and Y)..... (11*b*)

Calculate the weight in pounds per 108 sq. ft. of fine mineral matter admixed with the top coating (Type X) i.e. (7*a*)×(11*a*)..... (12*a*)

Calculate the weight in pounds per 108 sq. ft. of fine mineral matter admixed with the bottom coating (Types X and Y) i.e. (7*b*)×(11*b*)..... (12*b*)

Calculate the weight in pounds per 108 sq. ft. of fine mineral matter embedded in the top coating (Type X) i.e. (8*a*)−(12*a*)..... (13*a*)

Calculate the weight in pounds per 108 sq. ft. of fine mineral matter embedded in the bottom coating (Types X and Y) i.e. (8*b*)−(12*b*)..... (13*b*)

Compilation of Results.—The following items shall be reported in pounds per 108 sq. ft.:

	Type X	Type Y
Mineral Matter:		
Fine mineral matter embedded in top coating	Item (13*a*)	.....
Coarse or moderately coarse mineral matter embedded in top coating	.....	Item (9)
Fine mineral matter embedded in bottom coating	Item (13*b*)	Item (13*b*)
Fine mineral matter admixed with top coating	Item (12*a*)	Item (10)
Fine mineral matter admixed with bottom coating	Item (12*b*)	Item (12*b*)
Bituminous Matter:		
Contained in top coating	Item (7*a*)	Item (7*a*)
Contained in bottom coating	Item (7*b*)	Item (7*b*)
Saturant of the felt	Item (6)	Item (6)
Fibrous Matter:		
Felt after desaturation	Item (3)	Item (3)
Net weight of roofing material	Sum	Sum
Check total	(Item 1)	Item (1)
Detached mineral matter	Item (2)	Item (2)
Packing material, nails and cement	Weight	Weight
Gross weight per 108 sq. ft.	Sum	Sum
Per Cent Ash:		
From desaturated felt	Item (4)	Item (4)

If desired, the results may also be expressed in % by weight.

PART IV

EXAMINATION OF BITUMINOUS-SOLVENT COMPOSITIONS

(*A*) PHYSICAL TESTS OF FINISHED PRODUCT

The following tests have been proposed, concerning which the particulars will be found elsewhere.

Specific Gravity.
Viscosity.
Plasticity and Mobility.
Flash-point.
Spreading Capacity and Workability.
Draining Test.
Time of Drying.
Hiding Power.
Color.
Gloss.
Hardness, Abrasion and Adhesion.
Water Absorption.
Resistance to Heat.
Resistance to Oil.
Resistance to Acids and Alkalies.
Dielectric Strength.

(*B*) SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

Estimation and Recovery of the Solvent

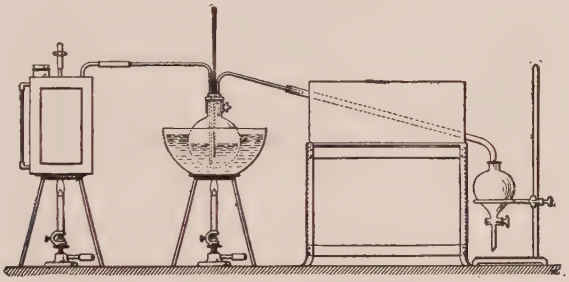
Steam Distillation Method.—This has been standardized as follows: The bituminous mixture is distilled in a current of steam, the solvent is condensed and separated from the water. The steam-generator shall be made of either metal or glass, with a capacity of from 2 to 4 liters, suitable for continued use in the production of steam. If of glass, it shall be fitted with two outlets with suitable connections for rubber tubing. In the case of a metal generator, a large opening for filling and a water gage shall be additional parts of the apparatus. The generator shall be supplied with suitable pinch cocks or valves so that steam may be blown off to the atmosphere until the test is ready. The bath shall be of metal of sufficient capacity to permit immersion of the distilling flask to a depth of not less than 10 cm. Heat for the steam generator shall be supplied by a suitable gas generator or electric hot plate. The bath may be heated by any convenient means.

The distilling flask shall be a short ring-neck, round-bottom flask of 1000-ml. capacity. It shall be fitted with a three-hole rubber stopper; with a steam distilling tube which will reach to within ½ in. (12.7 mm.) of the bottom of the flask and project from the top at a convenient distance for connection to the

generator; a vapor outlet tube which extends from beneath the rubber stopper to a point sufficiently above the distilling flask that will permit convenient connection to the condenser; and with a thermometer. The steam tubing should be not less than 2 nor more than 4 mm. in internal diameter and the vapor outlet tube should be not less than 5 mm. in internal diameter.

The condenser shall consist of a $\frac{9}{16}$-in. (14.29 mm.) outside diameter No. 20 Stubbs' Gauge seamless brass tube, 22 in. (55.88 cm.) long. It shall be set at an angle of 75° from the perpendicular and be surrounded with a cooling bath 15 in. (38.1 cm.) long, approximately 4 in. (10.16 cm.) wide by 6 in. (15.24 cm.) high. The lower end of the condenser tube shall be cut off at an acute angle, and curved downward for a length of 3 in. (7.62 cm.) and slightly backward so as to insure contact with the wall of the graduate at a point 1 to 1¼ in. (2.54 to 3.18 cm.) below the top of the graduate when it is in position to receive the distillate.

A separatory funnel having a capacity of not less than 500 ml. should be provided. Accessories consist of suitable ring stands for supporting the steam generator, distilling flask, bath for distilling flask, separatory funnel, and a thermometer.



Courtesy A.S.T.M.

Fig. 221.—Assembly of Distillation Apparatus.

The apparatus shall be assembled as shown in Fig. 221. The steam-generator shall be filled with water and heat applied. The bath shall be filled with a high-flash-point oil and raised to approximately 140° C. (284° F.) Five hundred milliliters of the sample shall be weighed into the round-bottom flask. The connection shall be made from the steam-generator to the steam delivery tube, the end of which shall be within ½ in. of the bottom of the distilling flask. The outlet from the distilling flask shall be connected to the condenser and the separatory funnel placed in position at the outlet of the condenser to receive the distillate. The end of the bulb of the thermometer in the steam-distilling flask shall be placed within ½ in. (12.7 mm.) of the bottom of the distilling flask.

When the temperature of the sample in the distilling flask reaches 130° C. the outlet of the steam generator shall be closed, thus forcing the steam to pass through the sample. The flow of steam shall be adjusted so that the distillate is collected at the rate of approximately 6 to 10 ml. per minute. The distillation shall be stopped when 100 ml. of the distillate contains not more than 0.5 ml. of solvent, as determined by measuring the amount of oil in 100 ml. of distillate.

When the distillation is finished, the water shall be separated from the distillate and the distillate measured and retained for further tests, if required by the specifications.

In some cases, the distillate does not separate readily from the water, and this separation can be facilitated by the addition of sodium chloride, which will result in a sufficient difference in gravity to produce a clear separation of the two layers.

The results shall be reported in per cent by weight or volume as required by the specifications, based on the weight of the sample taken.

NOTE.—In the distillation of varnishes the end point differs with the various types and compositions. In all cases, however, the rate of distillation slows down as the end point is approached; and, when the end point is reached, acrolein (formed in the decomposition of the varnish base) is evolved and may be detected by its characteristic odor.

In addition to the evolution of acrolein, the following phenomena are suitable indicators of end point:

(1) When the end point of the solvent is considerably lower than the initial boiling point of the base, the end point of the distillation is indicated by the temperature reaching a maximum and then starting to fall consistently.

(2) When the end point of the solvent and the initial boiling point of the base are too close, or overlap, the above temperature drop does not occur. The end point of the distillation is then indicated by a sudden foaming up of the residual base in the distillation flask; or, if the distillation has been accompanied by foaming, the end point is indicated by a breaking of surface tension with a consequent cessation of foaming.

The specific gravity of the volatile matter (solvent) recovered by distillation shall be determined in accordance with the procedure described below.

The difference between 100% and the percentage of non-volatile matter determined above shall be calculated and recorded as the percentage of volatile matter by weight.

The percentage of volatile matter by volume shall be calculated from the formula:

$$x = \frac{AC}{B}$$

where

x = the percentage of volatile matter by volume;
A = the specific gravity of the original varnish;
B = the specific gravity of the volatile matter (solvent) recovered by distillation,
C = the percentage of volatile matter by weight.

With proper care and attention to detail in making this test, differences occurring between different laboratories should not exceed 2% for varnishes containing solvents which have end points not over 235° C. (455° F.), and should not exceed 4% when the end point of the solvent is as high as 307.2° C. (585° F.).

To correct the loss of distillate for water-soluble constituents, weigh out another 100 g. into a 250-ml. flask and distil without steam over an electric stove. Continue the distillation until the residue in the flask reaches a temperature of 200° C. This gives somewhat lower results than the first method, but the distillate should be tested for water-soluble substances to correct the

results obtained by the previous method. Turpentine dissolves to the extent of 0.3 g. for each 100 ml. of water condensed.

If the residue is to be used for further examination, any water introduced into it by the steam distillation may be removed by distilling it twice with ten times weight of a mixture of 3 parts benzol and 1 part alcohol.

(*C*) ESTIMATION, RECOVERY AND EXAMINATION OF PIGMENT AND FILLER

Dilute 100 g. of the well-mixed material with 500 ml. of benzol in an 800-ml. stoppered flask. Either centrifuge or let stand in a warm place until the pigment or filler has settled, then carefully decant the supernatant liquid into a clean flask of large capacity. The pigment or filler is shaken up with 250 ml. more benzol, allowed to stand in a warm place until it settles, and the supernatant liquid decanted into the second flask. Repeat the treatment with benzol until the vehicle has been completely extracted from the pigment. The prevention of skin formation during this process may be attained by the addition of anti-oxidants such as phenol or hydrochinone (dissolved in ether), which are subsequently expelled on heating the pigment and base. The combined extracts are allowed to stand quietly to recover any pigment that may have been carried over with the benzol, and then carefully decanted through a weighed Gooch crucible provided with an asbestos filter. The residues in the flask and on the Gooch crucible are washed with benzol as before, and combined with the balance of pigment or filler, which is then dried at 110° C. and weighed. The combined extracts are retained for further examination.

The pigments or filler recovered from the previous test are subjected to a qualitative or quantitative analysis for purposes of identification likewise to granularmetric tests.

(*D*) ESTIMATION, RECOVERY AND EXAMINATION OF THE BASE

If no pigments or fillers are present, the base is recovered as described, and its percentage by weight ascertained directly. If pigments or fillers are present, the combined extracts are distilled to a small bulk, transferred to a tared dish, and evaporated in an oven at 110° C. *exactly* to the calculated weight of the base, by subtracting the weights of solvent and pigment or filler from the original weight of material taken for examination. When oxidizable substances are present, the final evaporation should take place in an atmosphere of illuminating gas.

The base will contain the bituminous constituents (with the exception of any "free carbon" associated with coal-tar pitch, or the like, which will be separated with the pigments and fillers), likewise animal and vegetable oils or fats, resins, and metallic bases and dryers. It may be separated into its component parts as follows:

Method of Analyzing the Separated Base

Dissolve 50 g. in 150 ml. benzol. Add 10 ml. dilute nitric acid (1 : 1) and boil under a reflux condenser for one-half hour to decompose any metallic soaps (*i.e.*, driers, etc.). Add 150 ml. water, boil under reflux condenser, transfer to a separatory funnel, draw off the aqueous layer, boil with another 100 ml. water, and repeat if necessary until all the metals are removed.

Benzol Solution:

Distil to 100 ml., add 300 ml. of the saponifying liquid *, boil under reflux condenser for one hour, and separate the unsaponifiable and saponifiable constituents as described.

Unsaponifiable Matter:

Examine a small portion. If higher alcohols are present, separate the balance into:

Hydrocarbons:

Contain the bituminous substances (*i.e.*, asphalt, coal-tar pitch, unsap. matter derived from fatty-acid pitch, etc.).

Higher Alcohols, Etc.:

Contain cholesterol, etc., derived from wool grease, also the unsaponifiable constituents originally present in resins (4 to 8%).

Saponifiable Matter:

Separate the fatty and resin acids as described.

Fatty Acids:

Include acids derived from vegetable and animal oils or fats, also from fatty-acid pitch.

Resin Acids:

Include acids derived from rosin and the fossil resins.

Aqueous Layer:

Determine percentage glycerol. Multiply this by 10 to estimate per cent of vegetable or animal oils or fats (triglycerides) present in the original substance.

Aqueous Extract:

Contains the metallic bases as nitrates. Examine qualitatively and then quantitatively for lead, manganese, cobalt, zinc, calcium, and magnesium.

(N.B.—The last three used for hardening rosin. The mettallic dryers should *not* be found by ignition, since the lead will be reduced to metal by the organic matter, and volatilized.)

* The saponifying liquid shall consist of a 10% solution of KOH dissolved in equal parts of 95% C_2H_5OH or 90% benzol.

PART V

EXAMINATION OF BITUMINOUS DISPERSIONS

(A) PHYSICAL TESTS OF FINISHED PRODUCT

Settlement Test

The following apparatus will be required:

(*a*) *Cylinders.*—Two glass cylinders of 500-ml. capacity with pressed or molded glass base and cork or glass stoppers. The outside diameter shall be 5.0 cm.±0.5 cm. and the cylinders shall be graduated at each 5-ml. interval to the 500-ml. mark.

(*b*) *Glass Pipette.*—A syphon, glass tube pipette, 60-ml. capacity, form optional.

A 500-ml. sample, representative of the emulsion, shall be placed in each of two glass cylinders. The cylinder shall be stoppered air-tight and stood aside unmolested, at laboratory air temperature for 5 days. After standing for this 5-day period, approximately the first 55 ml. of emulsion shall be removed by means of the pipette or syphon from the top of each cylinder without disturbing the balance of their contents. Exactly 50 g. of each of the two samples, after each has been thoroughly mixed separately, shall be weighed into separate 600-ml. low-form glass beakers and the asphaltic residue determined by evaporation at 325° F. (163° C.) for 3 hr. in the apparatus described.

After removal of the first sample, approximately the next 390 ml. shall be syphoned off from each of the cylinders. The residue remaining in the cylinders shall be mixed thoroughly and exactly 50 g. shall be weighed out from each of them and the amount of asphaltic residue (all sediment, if any, included) shall be determined by evaporation as described above for the two top samples.

The numerical difference between the average percentage of asphaltic residue from the two top samples and the average percentage found in the two bottom samples shall be recorded.

Demulsibility Test

This test indicates the rapidity with which the dispersion "breaks" during use, and may be ascertained in accordance with the following procedure:

The following apparatus and reagents will be required:

(a) **Sieves.**—Three No. 14 sieves of the U. S. Standard Sieve Series, of iron wire cloth, unframed, approximately 5-in. square.

(b) **Beakers.**—Three glass beakers of 600-ml. capacity each.

(c) **Glass Rods.**—Three glass rods, rounded ends, approximately $\frac{5}{16}$ in. in diameter.

(d) **Burette.**—A 50-ml. glass burette graduated in 0.1 ml.

(e) **Calcium Chloride Solution (0.02 N).**

(f) **Calcium Chloride Solution (0.10 N).**

The percentage of residue shall be determined by distillation as described on p. 1593.

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The weight of each assembly of beaker, rod and sieve shall be recorded. Exactly 100 g. of the emulsified asphalt shall be weighed into each of three 600-ml. tared beakers. Over a period of approximately 2 min., 35 ml. of 0.02 N $CaCl_2$ solution (if quick-setting emulsion is being tested) or 50 ml. of 0.10 N $CaCl_2$ solution (if mixing type emulsion is being tested) shall be added to each beaker from a burette. While adding the solution of $CaCl_2$, the contents of the beaker shall be stirred continuously and vigorously, kneading lumps against the sides of the beaker to insure thorough mixing of the reagent with the emulsion. This operation shall be performed after bringing the weighed sample of emulsion and the reagent to the standard temperature of 77° F.±1.0° F. (25° C.±0.5° C.).

One of the wire sieves shall be fitted over a beaker or other suitable vessel and the mixture of emulsion and reagent poured through the sieve. The beaker, containing the sample and glass rod, shall be rinsed with distilled water. All lumps shall be kneaded and broken up and the washing of the beaker, rod and sieve shall be continued until there is no longer any appreciable color imparted to the wash water. After washing as directed, the beaker, rod and sieve used in each individual test shall be placed in a drying oven and dried at 325° F. (163° C.) to constant weight.

The total weight thus obtained less the total tare weight of the beaker, rod and sieve shall be the weight of the residue by the demulsibility test. The ratio of the average weight in grams from three tests of each individual sample of emulsified asphalt, A, to the weight in grams of residue per 100 g. of emulsion, B, obtained in the test for residue by distillation described in Section 6 multiplied by 100, shall be recorded as the percentage of demulsibility of the sample tested:

$$\text{Percentage Demulsibility} = \frac{A}{B} \times 100$$

Effects of Freezing

Approximately 400 g. of the emulsion shall be placed in a clean metal container, such as a 1-pt. press-top tin. The emulsion in the closed container shall be exposed to a temperature of 0° F. (−17.7° C.) for twelve consecutive hours. At the expiration of the freezing period, the emulsion shall be permitted to thaw by exposure of the container to the temperature of the laboratory.

After the first operation of freezing and thawing, the procedure shall be repeated twice, so that the emulsion will have been subjected to three cycles of freezing and thawing.

After the third cycle, the emulsion may be homogeneous or may have separated into distinct layers which cannot be rendered homogeneous by stirring at laboratory temperature.

The result of this test shall be reported as either "Homogeneous" or "Broken."

(*B*) SEPARATION OF THE DISPERSION INTO ITS COMPONENT PARTS

The following products are likely to be present, viz.: water, ammonia, various chemicals, bituminous matter, animal and vegetable oils or fats, other forms of non-bituminous organic matter and mineral matter.

Distillation Residue.—The following method has been standardized:

The following apparatus will be required:

(*a*) ***Iron Still.***—The iron still shall be approximately 6 by 3½ in. in inside diameter with adjustable ring burner with holes on the inner periphery to fit around the outside of the still.

NOTE.—A modification of this still is shown in Fig. 222. It consists of the regular still with an expansion chamber superimposed thereon. Two additional ring burners are required, one approximately 6 in. in inside diameter with the holes bored on the inside periphery, and one approximately 2 in. in diameter with the holes bored on top.

(*b*) ***Connecting Apparatus.***—A connecting tube, tin shield, condenser trough, condenser tube and graduated cylinder, as shown in Fig. 223.

(*c*) ***Thermometer.***—A thermometer graduated from 30° to 580° F. (0 to 300° C.).

NOTE.—The details of the assembly of apparatus for the distillation test are illustrated in Fig. 223.

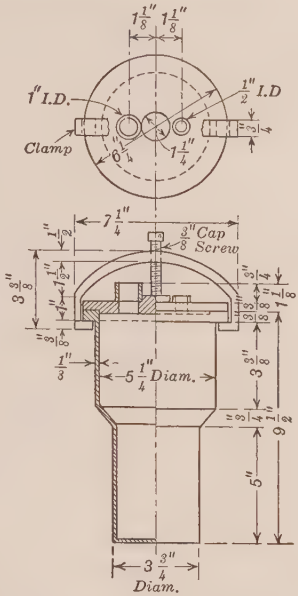


FIG. 222.—Iron Still for Use with Badly Foaming Emulsions.

Exactly 200 g. of a well-mixed and representative sample of the emulsion shall be placed in the previously weighed iron still (including lid, clamp, thermometer and gasket, if gasket is used). A gasket of oiled paper may be used between the still and its cover or the joint ground to a tight fit. The cover shall be clamped securely on the still. The thermometer shall be inserted

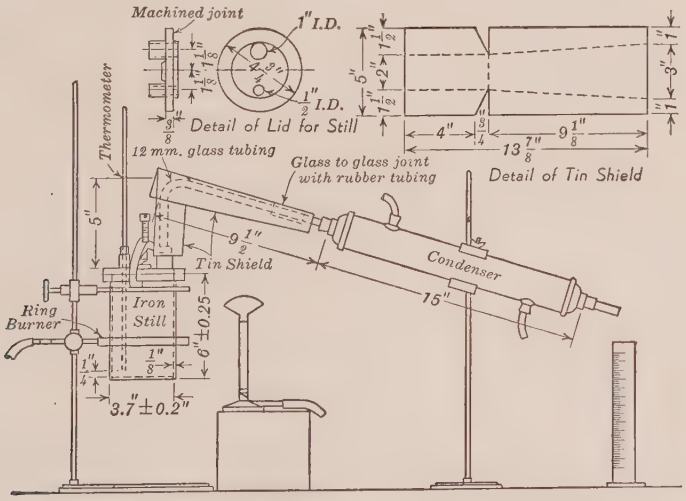


FIG. 223.—Apparatus Assembly for Distillation Test of Emulsified Asphalts.

through the small hole in the cover, using a cork stopper, so that the end of the bulb is ¼ in. from the bottom of the still. The ring burner shall be placed around the still and the heat applied by this means to the top of the still. Just enough heat from a bunsen burner shall also be applied to the connecting tube to prevent condensation of water in this tube.

After practically all the condensate has been removed from the still and the temperature of the residue has reached 250° F. (121° C.), the position of the heat from the ring burner shall be lowered to midway of the still and held there until the thermometer reaches 349° F. (176° C.). The burner shall then be rapidly lowered to within ¼ in. of the bottom of the still and the temperature increased to and maintained at 500° F. (260° C.) for 15 min. This latter period of heating is necessary to insure a smooth homogeneous residue in the still. At the expiration of the heating period at the maximum temperature, the still and accessories shall again be weighed and the percentage residue calculated and reported. The cover shall then be removed from the still and suitable portions of the residue shall be poured immediately into suitable molds and containers for making the required tests. The residue in the molds and containers shall be permitted to cool, uncovered, to laboratory room temperature and thereafter tested for specific gravity, penetration, ductility, fusing-point, solubility in carbon disulfide and ash.

It should be noted that the distillation residue will carry any non-volatile dispersing agents present in the emulsion.

Note.—When it appears impossible to distill an emulsified asphalt in the still described above due to excessive foaming of the emulsion, then the modified still shown in Fig. 222 should be substituted for the still shown in Fig. 223 and the following procedure followed: Place the 6-in. burner around the larger diameter of the still near its top. This serves as a support. Place the 4-in. burner immediately beneath the flare and the 2-in. burner not less than 2 in. below the bottom. Distillation is started with only the 2-in. burner lighted. Practically all of the distillate should be over in about 45 min. When the distillation apparently stops, light the two larger ring burners and adjust to a low flame. Distillation resumes and when it stops again increase the heat by adjusting the flame of the 2-in. burner. When the temperature can be read upon the thermometer, increase the rate of heating by raising the flame on both the 2 and 4-in. burners and bring the temperature to 500° F. (260° C.). If any evidence is noted of the emulsion beginning to foam over in the delivery tube, remove the 2-in. burner quickly and raise a pan of water so as to immerse the still bottom to a depth of about 2 in. for a moment which will check the foaming. Upon resumption of heating watch delivery tube carefully and repeat treatment if necessary.

When the residue has reached and remained at 500° F. (260° C.) for 15 min., proceed as described for the regular still. While the distillation should be completed in not less than 1 hr. nor more than 1¼ hr. from the first application of heat to the still, the maximum stated is not mandatory as a longer time may be required in some cases to avoid foaming of the emulsion into the condenser. If the residue in the still prior to pouring the ductility and penetration specimens appears granular or heterogeneous in any way, stir with a spatula until the material runs from the spatula in strings instead of drops, and then pour. Should the residue then appear granular and heterogeneous, the test shall be rejected and the distillation repeated as previously described with the exception that the still temperature at 500° F. (260° C.) shall be maintained for a longer time than 15 min. until the desired condition of the residue is obtained.

Water and Volatile Oils.—The following method has been standardized:

This method of test determines water existing in a sample of bituminous emulsion by distilling the sample with a volatile solvent.

(*a*) The apparatus shall consist of a metal still or glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the still or flask. The trap serves to collect and measure the condensed water and to return the solvent to the still. The type of distilling apparatus used is not an essential feature of this method.

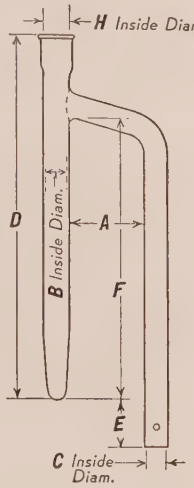
(*b*) ***Metal Still.***—The metal still shall be a vertical cylindrical vessel, preferably of copper, having a faced flange at the top to which the head is tightly attached by means of a clamp. The head shall be of metal, preferably of brass or copper, and be provided with a tubulation 1 in. in inside diameter.

(*c*) ***Glass Still.***—The glass flask shall be of the short neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

(*d*) ***Heat Source.***—The burner used with the metal still shall be a ring gas burner 100 mm. (4 in.) in inside diameter. With the glass flask, an ordinary gas burner or electric heater may be used as the source of heat.

(*e*) ***Condenser.***—The condenser shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length with an inner tube 9.5 to 12.7 mm. (⅜ to ½ in.) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30° from the vertical axis of the condenser.

(*f*) ***Trap.***—The trap shall be made of well-annealed glass constructed in accordance with Fig. 224, and shall be graduated from 0 to 25 ml. in 0.1-ml. divisions. The tolerance of the graduations between 0 and 2 ml. shall be ±0.5 ml. and between 2 and 25 ml. shall be ±0.1 ml. The outside diameters should be preferably 2.5 to 3.5 mm. ($\frac{3}{32}$ to ⅛ in.) greater than the inside diameters specified.



A = 45 to 55 mm.
B = 14 to 16 mm.
C = 12 to 16 mm.
D = 235 to 255 mm.
E = 23 to 38 mm.
F = 186 to 194 mm.
H = 18 to 19 mm.

FIG. 224.

The solvent used when testing bituminous emulsions shall be a coal-tar naphtha or a light oil and shall conform to the following distillation requirements:

98 per cent shall distil between 248° F. (120° C.) and 482° F. (250 C.)

The sample shall be thoroughly representative of the material to be tested and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement shall not be permitted.

NOTE.—The difficulties in obtaining proper representative samples for this determination are unusually great so that the importance of sampling cannot be too strongly emphasized.

When the material to be tested contains less than 25% of water, exactly a 100-g. sample shall be placed in the still or flask. When the material contains more than 25% of water, the sample shall be 50 g. The sample to be tested shall be thoroughly mixed with an equal volume of solvent by swirling, proper care being taken to avoid any loss of material.

The connections between the still or flask, trap and condenser shall be made by means of tight-fitting corks as shown in Fig. 210 (*a*) and (*b*). The end of the condenser inserted in the trap shall be adjusted to that position which will allow the end to be submerged to a depth of not more than 1 mm. (0.04 in.) below the surface of the liquid in the trap after distillation conditions have been established. When the metal still is used, a heavy paper gasket moistened with the solvent shall be inserted between the lid and flange before attaching the clamp. A loose cotton plug shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

Heat shall then be applied and so regulated that the condensed distillate falls from the end of the condenser at the rate of from 2 to 5 drops per sec. The ring burner used with the metal still shall be placed about 3 in. above the bottom of the still at the beginning of the distillation and gradually lowered as the distillation proceeds. The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. This operation usually requires less than 1 hr. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of distillation for a few minutes.

The volume of condensed water measured in the trap at room temperature multiplied by 100 and divided by the weight of sample used, shall be the percentage of water and shall be reported as ". . . per cent water by weight."

The accuracy to be expected with this method is that duplicate determinations of water should not differ from each other by more than one division on the trap.

The sum of the percentages of Distillation Residue and Water, deducted from 100 represents the percentage of Volatile Oils.

CEMENT

SPECIFICATIONS AND CHEMICAL ANALYSIS [1]

The physical tests ordinarily applied to Portland cement are as follows:

Setting time.
Soundness.
Tensile strength.[2]

Chemical analysis is also made, particular attention being paid to the determination of magnesia, sulfuric anhydride, insoluble residue, and loss on ignition. As a general rule, however, it may be said that so far as the consumer is concerned, more attention is paid to the physical tests than to chemical analysis.

Standard specifications covering the requirements for cement, both chemical and physical, have been adopted by the American Society for Testing Materials, and by the U. S. Government.[3] The former are generally recognized by cement users as the standard requirements, while the latter are used by the various branches of the federal government. The two sets of specification may be very different.

The specifications and methods of making the chemical tests follow.

SPECIFICATIONS [4]

Definition.—Portland cement is the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum.

Chemical Limits.—The following maximum limits shall not be exceeded by amounts greater than the respective tolerances indicated as allowable in the chemical determinations:

	Limits	Tolerance
Loss on ignition, %	4.00	0.25
Insoluble residue, %	0.85	0.15
Sulfuric anhydride (SO_3), %	2.00	0.10
Magnesia (MgO), %	5.00	0.40

[1] By W. C. Hanna, Chief Chemist and Chemical Engineer, California Portland Cement Co., Colton, California.

[2] See A. S. T. M. Method C 77–37 for the Physical Tests. 1937 Supplement to Book of A. S. T. M. Standards, pp. 61–73.

[3] The federal specifications are issued by the Director of Procurement, Washington, D. C., and sold by the Superintendent of Documents, Government Printing Office, Washington, D. C. The specifications now in effect covering cement are as follows:
SS–C–158. September 30, 1936. Cements, Hydraulic; General Specifications (Methods for Sampling, Inspection, and Testing).
SS–C–191a. September 30, 1936. Cement; Portland.
SS–C–201. September 30, 1936. Cement; Portland, High-Early-Strength.
SS–C–206. September 30, 1936. Cement; Portland, Moderate-Heat-of-Hardening.
SS–C–181a. May 22, 1936. Cement; Masonry.

[4] Standard Specifications for Portland Cement. A. S. T. M. Designation: C 9–37.

The residue on a standard No. 200 sieve shall not exceed 22% by weight.

A pat of neat cement shall remain firm and hard, and show no signs of distortion, cracking, checking, or disintegration in the steam test for soundness.

The cement shall not develop initial set in less than 45 minutes when the Vicat needle is used or in less than 60 minutes when the Gillmore needle is used. Final set shall be attained within 10 hours.

The average tensile strength in pounds per square inch of not less than three standard mortar briquettes composed of one part cement and three parts standard sand, by weight, shall be equal to or higher than the following:

Age at Test, Days	Storage of Briquettes	Tensile Strength, lb. per sq. in.
7	1 day in moist air, 6 days in water.....	275
28	1 day in moist air, 27 days in water.....	350

The average tensile strength of standard mortar at 28 days shall be higher than the strength at 7 days.

Packages and Marking.—The cement shall be delivered in packages as specified with the brand and name of the manufacturer plainly marked thereon, unless shipped in bulk. When shipped in bulk, this information shall be contained in the shipping advices accompanying the shipment. A bag shall contain 94 lb. net. A barrel shall contain 376 lb. net. All packages shall be in good condition at the time of inspection.

The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment, and in a suitable weather-tight building which will protect the cement from dampness.

Inspection.—Every facility shall be provided the purchaser for careful sampling and inspection at either the mill or at the site of the work, as may be specified by the purchaser. At least 12 days from the time of sampling shall be allowed for the completion of the 7-day test, and at least 33 days shall be allowed for the completion of the 28-day test. The cement shall be tested in accordance with the methods hereinafter prescribed. The 28-day test need not be made if waived by the purchaser.

Rejection.—The cement may be rejected if it fails to meet any of the requirements of these specifications.

Cement remaining in storage prior to shipment for a period greater than 6 months after completion of the tests shall be retested and shall be rejected if it fails to meet any of the requirements of these specifications.

Cement failing to meet the test for soundness in steam may be accepted if it passes a retest using a new sample at any time within 28 days thereafter. The provisional acceptance of the cement at the mill shall not deprive the purchaser of the right of rejection on a retest of soundness and time of setting at the time of delivery of cement to the purchaser.

Packages varying more than 5% from the specified weight may be rejected; and if the average weight of packages in any shipment, as shown by weighing 50 packages taken at random, is less than that specified, the entire shipment may be rejected.

Methods of Testing.—The cement shall be sampled and tested in accordance with the Standard Methods of Sampling and Testing Portland Cement (A. S. T. M. Designation: C 77) of the American Society for Testing Materials.

STANDARD METHODS OF SAMPLING AND TESTING PORTLAND CEMENT [5]

A. S. T. M. Designation: C 77–37 [6]

SAMPLING

Size and Number of Samples.—1. Samples for purpose of tests shall weigh at least 4 lb.

2. Test samples shall be either individual or composite samples, as may be ordered, and one test sample shall represent not more than 300 bbl., unless otherwise specified by the purchaser.

Methods of Sampling.—3. When cement is sampled in cars, trucks, boats, warehouses, etc., one sample shall be taken from one sack in each 40 sacks (one sample per 10 bbl.), and combined to form one test sample. In the case of truck samples where the cement is being trucked from one mill, it is permissible to combine the samples from several trucks to form a test sample representing not more than 300 bbl. When sampling bulk shipments, representative samples shall be taken from well distributed points.

Sampling Bulk Storage.—4. The cement may be sampled at bulk storage points by any of the following methods:

(*a*) ***From the Conveyor Delivering to Storage.***—At least 4 lb. of cement shall be taken from at least each 300 bbl. passing over the conveyor. This may be secured by taking the entire test sample at a single operation, known as the "Grab Method," or by combining several portions taken at regular intervals, known as the "Composite Method." When obtaining a composite sample this shall be secured by combining approximately equal weights taken at regular intervals, each portion representing approximately 10 bbl. Automatic samplers may be used in obtaining samples.

[5] Under the standardization procedure of the Society these methods are under the jurisdiction of the A. S. T. M. Committee C-1 on Cement.

A Manual of Cement Testing to supplement these methods has been prepared and published as information, not a part of these methods, see *Proceedings*, Am. Soc. Testing Mats., Vol. 32, Part I, p. 316 (1932).

[6] These methods are issued under the fixed designation C 77; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Adopted, 1904; Issued in Amended Form Under Present Designation, 1930; Revised, 1932, 1937. Reproduced with the permission of the American Society for Testing Materials.

(*b*) ***From Storage by Means of Proper Sampling Tubes.***—Tubes inserted vertically may be used for sampling cement to a maximum depth of 10 ft. Tubes inserted horizontally may be used where the construction of the storage permits. Samples shall be taken at points well distributed over the storage.

(*c*) ***From Storage at Points of Discharge.***—Sufficient cement shall be drawn from the discharge openings to obtain samples representative of the cement, as determined by the appearance at the discharge openings of indicators placed on the surface of the cement directly above these openings before the drawing of the cement is started. One 4-lb. sample shall be taken for at least each 300 bbl.

Preparation of Sample.—5. The sampling shall be done by or under the direction of a responsible representative of the purchaser.

6. Samples shall be shipped and stored in moisture-proof, air-tight containers. Before testing, samples shall be thoroughly mixed and then passed through a No. 20 sieve in order to break up lumps and remove foreign materials.

CHEMICAL ANALYSIS [7]

Number of Determinations.—7. (*a*) When cement is sampled in accordance with Section 3 at least one determination of loss on ignition, insoluble residue content and magnesia content shall be made for each 10 test samples taken, and at least one determination of sulfuric anhydride (SO_3) content shall be made for each 3 test samples. In case of truck deliveries and car deliveries the sulfuric anhydride (SO_3) content shall be determined on each test sample. When the total number of test samples taken is less than either of the groups above specified at least one determination shall be made for each chemical requirement.

(*b*) When cement is sampled in accordance with Section 4 at least one determination of loss on ignition, insoluble residue content and magnesia content shall be made for each 15 test samples and at least one determination of sulfuric anhydride (SO_3) content shall be made for each 3 test samples; provided that at least one determination for each chemical requirement shall be made on each bin sampled.

(*c*) The chemical determinations may be made either on composites of the original test samples or may be made on individual test samples selected at random at the option of the purchaser.

(*d*) The chemical determinations shall be made in accordance with the procedure described in the following Sections 8 to 17 (Note).

NOTE.—This method of chemical analysis is not considered as possessing the highest obtainable accuracy, but is an acceptance method to be followed in making acceptance tests on cements covered by specifications requiring that tests be made in accordance with the analytical procedure contained in this standard.

Loss on Ignition.—8. Heat a 1-g. sample of cement in a weighed covered platinum crucible of 20 to 25-ml. capacity, as follows, using either Method 1 or 2 as specified.

(*a*) ***Method 1.***—Place the crucible in a hole in an asbestos board, clamped horizontally, so that about three fifths of the crucible projects below the board,

[7] This method of chemical analysis is very similar to that prepared by the National Bureau of Standards and adopted by the U. S. Department of the Interior, Bureau of Reclamation, in Specifications No. 566. Very few revisions have been made.

and heat at a full red heat (900° to 1000° C.) for 15 min.; check the loss in weight by a second heating for 5 min. Take care to wipe off particles of asbestos that may adhere to the crucible when withdrawn from the hole in the board. Greater neatness and shortening of the time of heating may be secured by making a hole to fit the crucible in a circular disk of sheet platinum and placing this disk over a somewhat larger hole in an asbestos board.

(*b*) ***Method 2.***—Place the crucible in a muffle furnace at any temperature between 900° and 1000° C. for 15 min. and check the loss in weight by a second heating for 5 min.

Insoluble Residue.—9. Add 25 ml. of cold water and 5 ml. of HCl (sp.gr. 1.19) to a 1-g. sample of cement. Heat the solution and grind the material with the flattened end of a glass rod until it is evident that decomposition of the cement is complete. Dilute the solution to 50 ml. and digest on a steam bath for 15 min. Filter the residue, wash six times with hot water, and digest the filter paper and contents in about 30 ml. of a sodium carbonate solution (5%), the liquid being held at a temperature just short of boiling for 15 min. Filter the remaining residue, wash twice with hot water, then with a few drops of hot diluted HCl (1 : 9), and finally eight to ten times with hot water, then ignite at a red heat and weigh as the insoluble residue.

Sulfuric Anhydride.—10. Add 25 ml. of cold water and 5 ml. of HCl (sp.gr. 1.19) to a 1-g. sample of cement. Heat the solution and grind the material with the flattened end of a glass rod until it is evident that decomposition of the cement is complete. Dilute the solution to 50 ml. and digest on a steam bath for 15 min., filter, and wash the residue thoroughly with hot water. Dilute the solution to 250 ml., heat to boiling, add slowly, drop by drop from a pipette, 10 ml. of a hot barium chloride solution (10%), and continue the boiling until the precipitate is well formed. Then digest the solution on the steam bath for at least 3 hr., preferably overnight. Filter the precipitate, wash and place the paper and contents in a weighed platinum crucible and slowly char and consume the paper without flaming. Then ignite, and weigh the barium sulfate. The weight obtained multiplied by 34.3 gives the percentage of sulfuric anhydride. The acid filtrate obtained in the determination of the insoluble residue may be used for the estimation of sulfuric anhydride instead of using a separate sample.

Silica.—11. (*a*) Transfer a 0.5-g. sample of the finely powdered cement to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moisten with 10 ml. of cold water to prevent lumping add 5 to 10 ml. of HCl (sp.gr. 1.19) and digest with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod. Evaporate the solution to dryness on a steam bath. Treat the residue without further heating at first with 5 to 10 ml. of HCl (sp.gr. 1.19) then diluting to half strength or less, or pour at once upon the residue a larger volume of acid of half strength. Then cover the dish and digest for 10 min. on the bath or a hot plate. Dilute the solution with an equal volume of hot water, immediately filter, and wash the separated silica thoroughly with hot water and reserve. Again evaporate the filtrate to dryness, baking the residue in an oven 1 hr. at a temperature of 105° to 110° C. Then take up the residue with 10 to 15 ml. of diluted HCl (1 : 1) and heat on the bath or hot plate. Dilute the solution with an equal volume of hot water and catch and wash the small amount of silica it contains on another filter paper. Reserve the filtrate and

washings. Transfer this paper and the reserved paper containing the residues to a weighed platinum crucible, dry, ignite first over a bunsen burner until the carbon of the filter paper is completely consumed without flaming and finally over a burner or in an electric oven at 1100° to 1200° C. until the weight remains constant.

(*b*) Treat the silica thus obtained, which will contain small amounts of impurities, in the crucible with a few drops of water, about 10 ml. of HF and one drop of H_2SO_4 and evaporate to dryness over a low flame. Finally, heat the small residue at 1050° to 1100° C. for a minute or two, cool, and weigh. The difference between this weight and the weight previously obtained represents the amount of silica. Washing of the silica precipitates can be made more effective by using a hot solution of diluted HCl (1 : 99), and then completing the washing with hot water. Consider the weighed residue, remaining after volatilization of the silica, as combined aluminum and ferric oxides and add it to the result obtained in the determination of these oxides (Section 12).

Ferric Oxide and Alumina.—12. Treat the reserved filtrate (Note 1), which should have a volume of about 250 ml., with HCl, if necessary, to insure a total of 10 to 15 ml. of the acid, add a few drops of methyl red indicator and then heat to boiling. Then treat with NH_4OH (Note 2), drop by drop, until one drop changes the color of the solution to a distinct yellow. Bring to boiling the solution containing the precipitated iron and aluminum hydroxides, boil for 1 or 2 min., and then filter. Wash the precipitate once by decantation and slightly on the filter with a hot ammonium nitrate solution (2%). Set aside the filtrate and transfer the precipitate and filter paper to the same beaker in which the first precipitation was effected. Then dissolve the iron and aluminum hydroxides in hot diluted HCl (1 : 3), make up the solution to about 100 ml., and reprecipitate the hydroxides as in the first case. Then filter the solution and wash the precipitate with two 10-ml. portions of a hot ammonium nitrate solution (2%). Combine the filtrate and washings with that set aside and place the precipitate in a weighed platinum crucible, slowly heat by a bunsen or Meker burner until the papers are charred, and finally ignite to constant weight at 1050° to 1100° C. with care to prevent reduction, and weigh as $Al_2O_3+Fe_2O_3$.

Notes.—1. If a platinum evaporating dish has been used for the dehydration of silica, iron may have been partially reduced. At this stage, add about 3 ml. of saturated aqueous solution of bromine to the filtrate and boil the filtrate to eliminate the excess bromine before adding the methyl red indicator.

2. The NH_4OH used to precipitate the hydroxides must be free of contamination with carbon dioxide.

Ferric Oxide.—This method for determining ferric oxide is not affected by any titania or vanadium oxide that may be in the cement. It is therefore understood that these are counted as Al_2O_3 in this method. If the precipitations of aluminum and iron are made as directed, little if any manganese will be retained in the precipitate.

Solutions Required.—13. The following solutions will be required:

(*a*) ***Stannous Chloride.***—Dissolve 2 g. of the crystallized salt in four times its weight of a mixture of three parts of water and one of HCl (sp.gr. 1.19). Add scraps of iron-free granulated tin and boil until the solution is clear. Keep the solution in a closed dropping bottle containing metallic tin.

(*b*) ***Phosphoric Acid Mixture.***—Add slowly and with stirring 150 ml. of orthophosphoric acid (sp.gr. 1.71), and 150 ml. of H_2SO_4 (sp.gr. 1.84), to 500 ml. of water and then dilute to 1000 ml. with water and mix.

(*c*) ***Diphenylamine Indicator.***—Dissolve 1 g. of diphenylamine in 100 ml. of H_2SO_4 (sp.gr. 1.84).

(*d*) ***Standard Potassium Bichromate Solution.***—Dissolve 2.457 g. of $K_2Cr_2O_7$ in distilled water and dilute to 1 liter. Standardize against standard iron wire of known iron content in the same manner as directed for the ferric oxide determination in cement (Section 14), using a weight of iron wire which will yield a titration approximately equal to that required by the cement sample in question.

Method.—14. Add 20 ml. of cold water and 10 ml. of HCl (sp.gr. 1.19) to a 1-g. sample of cement. Heat the solution and grind the material with the flattened end of a glass rod until it is evident that decomposition of the cement is complete. Dilute the solution to 50 ml. and heat to boiling. Then treat the solution with 5 ml. of HCl (sp.gr. 1.19) and then with a solution of stannous chloride, added drop by drop while stirring until the solution is decolorized, then add one drop more. Cool the solution to room temperature, rinse the inside of the vessel with water and add all at once 10 ml. of a cool saturated solution of mercuric chloride. Then stir the solution vigorously for 1 min., treat with 15 ml. of phosphoric acid mixture and three drops of indicator and dilute to 150 ml. with cold water. Then titrate with a standard potassium dichromate solution having a titer no greater than 0.004 g. of Fe_2O_3. The end point is taken as the point when a drop causes an intense deep-blue coloration that remains unchanged on the further addition of the standard $K_2Cr_2O_7$ solution.

Calcium Oxide.—15. Add a few drops of NH_4OH to the combined filtrates obtained in the alumina and ferric oxide precipitation (Section 12) and bring the solution to boiling. Add to the boiling solution 25 ml. of a boiling ammonium oxalate solution (5%), the boiling being continued until the precipitated calcium oxalate assumes a well-defined granular form. Then allow the solution to stand for about 20 min. or until the precipitate has settled, filter, and moderately wash with an ammonium oxalate solution (0.1%). Reserve the filtrate and washings. Place the filter paper containing the precipitate, wet, in a platinum crucible and burn off the paper over the small flame of a bunsen burner. Then ignite the precipitate until the oxalate is converted to oxide (Note), redissolve in HCl and make up the solution to 100 ml. with water. Add NH_4OH in slight excess and bring the solution to boiling. If a small amount of alumina separates at this point, filter it out, weigh, and add the amount to that found in the original alumina determination (Section 12). Then reprecipitate the lime by ammonium oxalate, allow to stand until settled, filter and wash, taking care to avoid an excess of the washing solution. Combine the filtrate with that already reserved. Weigh the precipitate as calcium oxide after ignition and blasting to constant weight in a weighed, covered platinum crucible.

Note.—If the ignited precipitate is darkly colored, it may contain an appreciable amount of manganese. The contamination of the second precipitate of calcium oxalate by manganese should be as low as possible. The following procedure may be used to reduce the contamination: add 5 ml. of cold water cautiously to the precipitate and then

cautiously add 10 ml. of diluted HCl (1 : 1). Heat the mixture. If the resulting solution is colored, digest it on the hot plate gently for 10 min. or longer until the color disappears or until it is apparent the color will not become lighter on further heating. After a little practice it is possible to dissolve hard-burnt lime in this way without explosive spattering.

If the second precipitate of calcium oxalate is so fine as to cause difficulty in filtering or if the precipitate causes bumping, the volume of solution may be increased to 150 or 200 ml., instead of 100 ml. prior to precipitation.

Magnesia.—16. In this method for determining magnesia, most of any manganese in the cement is precipitated with the magnesium. It is understood in this method that manganese so precipitated shall be calculated as magnesium.

Acidify the filtrates reserved in the determination of calcium oxide (Section 15) with HCl and concentrate to about 150 ml. Add to this solution about 10 ml. of diammonium phosphate solution (25 g. of the salt per 100 ml. of water) and boil the solution for several minutes. Then cool the solution by placing in a beaker of ice water. After cooling, add NH_4OH drop by drop, while stirring constantly, until the crystalline ammonium-magnesium orthophosphate begins to form, and then in moderate excess (5 to 10% of the volume of the solution), the stirring being continued for several minutes. Set the solution aside for at least 8 hr. in a cool atmosphere, and then filter. Redissolve the precipitate thus obtained in hot diluted HCl (1 : 4), make up the solution to about 100 ml., add 1 ml. of the solution of diammonium phosphate, and NH_4OH drop by drop, while stirring constantly until the precipitate is again formed as described, and the ammonia is in moderate excess. Then cool, allow to stand for about 2 hr., filter, and wash with two 10-ml. portions of wash solution (200 ml. of concentrated NH_4OH, 100 g. of ammonium nitrate, and 800 ml. of water), place in a weighed platinum crucible, slowly char the paper, and carefully burn off the resulting carbon. Ignite the precipitate at a temperature between 1100° and 1200° C. to constant weight, taking care to avoid bringing the pyrophosphate to melting. The weight of magnesium pyrophosphate obtained multiplied by 72.4 gives the percentage of magnesia.

Blank Determination.—17. Make a blank determination for sulfuric anhydride, silica, ferric oxide and alumina, ferric oxide, calcium oxide, and magnesia, using the same procedures as outlined in Sections 8 to 16, and using approximately the same amounts of reagents. Correct accordingly the results previously determined.

Balances.—18. The balances used in the chemical determinations shall conform to the following requirements:

(*a*) Capacity not less than 100 g. in each pan;

(*b*) The two arms of beam to be equal to within one part in 100,000;

(*c*) Capable of reproducing results within 0.1 mg.;

(*d*) "Sensibility reciprocal" [8] not more than 0.2 mg. per division of the graduated scale.

[8] The sensibility reciprocal is a measure of the sensitivity of a balance, and is the weight required to move the position of equilibrium of the beam, pan, pointed, or other indicating device of a scale a definite amount at the capacity or at any lesser load. For a complete definition of sensibility reciprocal, see Bureau of Standards *Handbook*, *M* 85, pp. 80–82.

(*e*) The weights used in the chemical determinations shall conform to the requirements of the National Bureau of Standards specifications for Class "S" weights as contained in Bureau of Standards *Circular No. 3*.

TENTATIVE METHOD OF CHEMICAL ANALYSIS OF PORTLAND CEMENT [9]

A. S. T. M. Designation: C 114–37 T [10]

METHOD A. ACID–ALKALI METHOD FOR RAPID DETERMINATION OF MAGNESIA [11]

Solutions Required.—1. The following solutions will be required:

(*a*) ***Trinitrobenzene Indicator.***—Dissolve 1.0 g. of C.P. 1–3–5 trinitrobenzene in 100 ml. of ethyl alcohol (95 to 100%).

(*b*) ***Phenolphthalein Indicator.***—Dissolve 0.4 g. of C.P. phenolphthalein in 100 ml. of ethyl alcohol (50%).

(*c*) ***Standard Sodium Hydroxide Solution.***—Dissolve 13.0 g. of sodium hydroxide in water, add 10 ml. of a freshly filtered saturated barium hydroxide solution, and dilute to 1 liter with distilled water which has been recently boiled and cooled. Shake the solution from time to time for several hours, and filter into a tubulature bottle fitted with an automatic burette. Protect the solution from carbon dioxide in the air, with soda-lime tubes at the top of the bottle and the burette.

The solution as prepared is approximately $\frac{1}{3}$ N, and shall be standardized against acid potassium phthalate or benzoic acid acidimetric standards furnished by the National Bureau of Standards (Standard Samples Nos. 84 and 39), using the methods in the certificates accompanying the standard samples. The exact normality of the solution shall be determined, and its MgO equivalent calculated on the basis that 1 ml. of a normal solution is equivalent to 0.02016 g. of MgO.

(*d*) ***Standard Acid Solution.***—Dilute 32.0 ml. of HCl (sp.gr. 1.19) or 26.0 ml. of HNO_3 (sp.gr. 1.42) to 1 liter with distilled water. This solution

[9] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee C-1 on Cement.

[10] This is a *Tentative Standard* and under the Regulations of the Society is subject to annual revision. Suggestions for revision should be addressed to the Headquarters of the Society, 260 S. Broad St., Philadelphia, Pa. Issued, 1934; Revised, 1935., 1937. Reproduced with the permission of the American Society for Testing Materials.

[11] This procedure is a modification of the method originally published by Fred P. Diener in *Concrete*, **39**, No. 6, December, 1931. The changes, which are in minor details and do not affect the underlying principles of the method, were made by the author in cooperation with the Working Committee on Methods of Chemical Analysis of Cement of the A. S. T. M. Committee C-1 on Cement for use in the investigations sponsored by the working committee. The theory of the method is discussed in the original article.

will be slightly in excess of ⅓ N, and shall be standardized against the standard sodium hydroxide solution, using phenolphthalein indicator, and adjusted by dilution until the two solutions are of equal strength.

(*e*) ***Potassium Iodide—Starch Paper.***—Mix equal volumes of a 5% potassium iodide solution and a 1% soluble starch solution, and dip strips of filter paper into the mixture.

Method.—2. (*a*) To 5.0 g. of cement in a 600-ml. beaker shall be added about 50 ml. of water and 50 ml. of HCl (1 : 1), and the solution boiled until the cement is completely in solution, excepting possibly some silica which may separate out (Note 1). Then 5 ml. of saturated bromine water shall be added and the boiling continued until the excess bromine is completely expelled, as indicated by the absence of a blue coloration on potassium iodide-starch paper when held in the issuing steam. The solution shall then be diluted to about 250 ml. with hot water and a 20% solution of sodium hydroxide added to the boiling solution from a pipette, until the excess acid is neutralized and a permanent precipitate just forms. Then, continuing the boiling, HCl (1 : 1) shall be carefully added from a pipette until the precipitate dissolves and the solution assumes a yellow ferric chloride color, avoiding much excess acid. The sides of the beaker shall be washed down with hot water and the boiling continued for a minute or two, and then the beaker shall be removed from the burner.

(*b*) To the solution shall be cautiously added 4.0 g. of calcium carbonate (weighed to the nearest 0.1 g.). This amount should be sufficient to completely neutralize the acid, with some excess. The solution shall then be diluted to about 400 ml. with hot water and boiled vigorously for 10 min. The solution shall be removed from the burner, and a 0.5% potassium permanganate solution carefully added to the hot solution from a burette, with vigorous stirring, until the supernatant liquid shows a faint pink color after settling for a moment. Avoid use of more permanganate than necessary to produce a faint pink color. Then the boiling shall be continued for 2 min., 2.0 ml. of ethyl alcohol added, and the boiling continued for a few minutes or until the pink color has disappeared (Note 2).

(*c*) The contents of the beaker shall then be transferred to a 500-ml. volumetric flask, cooled to room temperature, diluted to the mark, and mixed by shaking. The solution shall be filtered through a dry paper, and after discarding the first 10 or 20 ml. of filtrate, 200 ml. of the filtrate shall be transferred with a pipette to a 500-ml. Erlenmeyer flask. The solution in the flask shall be heated to boiling, and 3.0 ml. of trinitrobenzene indicator added. Then standard sodium hydroxide sloution shall be added 1.0 ml. at a time with intermittent boiling for a few seconds, until the magnesium is completely precipitated and a definite pink color persists on boiling. The total amount of alkali used shall be recorded (Note 3).

(*d*) The solution shall be transferred to a 250-ml. volumetric flask, cooled to room temperature, diluted to the mark, and mixed by shaking. The solution shall be filtered through a dry paper, into a graduated cylinder, discarding the first 10 or 20 ml. of filtrate, until 125 ml. of filtrate are secured. The 125 ml. of filtrate shall be transferred to a flask, a few drops of phenolphthalein indicator added, and the solution titrated with standard acid solution to the disappearance of the pink color.

(*e*) **Calculation.**—If the acid and alkali solutions are of equal strength, the quantity of alkali in milliliters minus twice the quantity of acid in milliliters is equivalent to the MgO in a 2-g. sample:

$$\text{MgO, per cent} = \frac{100(a-2b)}{2} \times \text{MgO equivalent of 1 ml. standard alkali,}$$

where a = the quantity of standard alkali in milliliters;
b = the quantity of standard acid in milliliters.

(*f*) **Blank Determination.**—A blank determination shall be made, using the same procedure as outlined above, and using approximately the same amounts of reagents. The titration results shall be corrected accordingly.

NOTES.—1. Some samples of cement, particularly those containing considerable iron or manganese, may require longer boiling or the addition of slightly more HCl to effect complete solution.

2. The purpose of the addition of potassium permanganate is to remove manganese from the sample, which otherwise would be precipitated and reported as MgO. The permanganate in a hot solution oxidizes the manganese to insoluble MnO_2 and is itself reduced to MnO_2. The ethyl alcohol precipitates the excess permanganate. In samples containing little or no manganese, this portion of the procedure may be omitted.

3. Enough standard alkali should be added to completely precipitate the magnesium without too large an excess which might cause some precipitation of calcium. A guide to proper procedure is the amount of back titration with acid, which should be held between 1.0 and 2.0 ml. (after being doubled). A little experience with the color change of the trinitrobenzene indicator will enable the operator to hold the back titration between these limits.

METHOD B. RAPID DETERMINATION OF MAGNESIA BY TITRATION OF MAGNESIUM OXYQUINOLATE [12]

Solutions Required.—3. The following solutions will be required:

(*a*) *8-Hydroxyquinoline (1.25%).*—Dissolve 25 g. of 8-hydroxyquinoline in 60 ml. of glacial acetic acid. When the solution is complete dilute to 2 liters with cold water. One milliliter of this solution is equivalent to 0.0016 g. of MgO.

(*b*) *Sodium Thiosulfate Solution (0.1 N).*—Dissolve 25 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 200 ml. of water and dilute to 1 liter. Standardize this solution either on sodium oxalate through a permanganate solution, or on arsenious oxide through a solution of resublimed iodine. Standard Samples Nos. 40 and 83 of the

[12] This procedure is a modification of the procedure originally published by J. C. Redmond in the Bureau of Standards Journal of Research, **10**, No. 6, June, 1933. The revision was made after correspondence with Mr. Redmond and for use in investigations sponsored by the Working Committee on Methods of Chemical Analysis of Cement of the A. S. T. M. Committee C-1 on Cement. The revised procedure differs from the original one mainly in two respects: (1) The hydrates of iron and aluminum are precipitated twice instead of once; and (2) the amounts of 8-hydroxyquinoline reagent and standard bromate solution used are variable instead of fixed.

The original article should be consulted for a discussion of the theory and experimental basis of the method. The method was developed primarily for use by the National Bureau of Standards for the detection of cements whose magnesia content did not meet the requirements of Federal Specifications Board Specification No. 1a. For use in the investigations of the working committee, the method was so revised that the magnesia content of any cement might be determined rapidly and correctly.

National Bureau of Standards are convenient for this purpose. One milliliter of exactly 0.1 N sodium thiosulfate solution is equivalent to 0.000504 g. of MgO.

(*c*) ***Potassium Bromate—Potassium Bromide Solution (0.2 N).***—Dissolve 20 g. of KBr and 5.57 g. of $KBrO_3$ in 200 ml. of water and dilute to 1 liter. Obtain the ratio of this solution to the standard sodium thiosulfate solution as follows: To 200 ml. of water in a 400-ml. beaker add exactly 25 ml. of bromate solution. Add 20 ml. of HCl (sp.gr. 1.19), stir, and add immediately 10 ml. of KI solution. Mix well and titrate at once with the sodium thiosulfate solution until nearly colorless. Add 2 ml. of starch solution, and titrate to the disappearance of the blue color.

(*d*) ***Potassium Iodide Solution (25%).***—Dissolve 25 g. of KI in 100 ml. of water.

(*e*) ***Starch Solution.***—To 500 ml. of boiling water add a cold suspension of 5 g. of soluble starch in 25 ml. of water, cool, add a cool solution of 5 g. of NaOH in 50 ml. of water, add 15 g. of KI and mix thoroughly.

Method.—4. (*a*) To a 0.500-g. sample of cement in a 400-ml. beaker shall be added 10 ml. of water and 10 ml. of HCl (sp.gr. 1.19). This shall be heated gently and any coarse particles ground with the flattened end of a glass rod until decomposition is complete. Hot water shall then be added to make a total volume of 100 ml.

(*b*) Three drops of methyl red (0.02 alcoholic solution) shall be added to the solution and then NH_4OH (sp.gr. 0.90) added until the solution is distinctly yellow. This solution shall then be heated to boiling and boiled for 1 to 2 min., then removed from the hot plate and allowed to stand until the precipitate has settled. The solution shall then be filtered without delay and the precipitate washed twice with a hot solution (2%) of ammonium chloride. The precipitate shall then be transferred with the filter paper to the beaker and dissolved in 10 ml. of HCl (1 : 1). This shall be diluted to about 100 ml. and heated to boiling. The hydrates shall then be reprecipitated, filtered, and washed as above. To the filtrate shall be added 1 ml. of NH_4OH (sp.gr. 0.90). The filtrate shall then be heated to boiling and while boiling 25 ml. of a hot solution (4%) of $(NH_4)_2C_2O_4 \cdot H_2O$ shall be added and the boiling continued for 2 min. The digestion shall be continued on the steam bath for 10 to 15 min.

(*c*) The solution shall be cooled to 70° C. and 10 to 25 ml. of the 8-hydroxyquinoline reagent added (Note 1) and then 4 ml. of NH_4OH (sp.gr. 0.90) added per 100 ml. of solution. The solution shall be stirred on a mechanical stirring machine for 15 min. and set aside until the precipitate has settled (Note 2). The solution shall then be filtered and the precipitate washed with hot dilute NH_4OH (1 : 40). The precipitate shall then be dissolved in 50 to 75 ml. of the hot dilute HCl (1 : 9), the resulting solution diluted to 200 ml. and then 15 ml. of HCl (sp.gr. 1.19) added. The solution shall then be cooled to 25° C. and 10 to 35 ml. of standard bromate solution (Note 3) added from a pipette. The solution shall then be stirred and allowed to stand for about 30 sec. to insure complete bromination. To this solution shall then be added 10 ml. of the KI solution. The resulting solution shall be stirred well and then titrated with the standard sodium thiosulfate solution until the color of the iodine becomes faintly yellow. At this point 2 ml. of the starch solution shall be added and the solution titrated to the disappearance of the blue color.

(*d*) **Calculation.**—The percentage of magnesia in a 0.5-g. sample may be calculated as follows:

$$\text{Percentage of MgO} = [(B-C)\times A] \times 200,$$

where A = the weight of MgO in grams per milliliter of standard sodium thiosulfate solution;
B = milliliters of standard sodium thiosulfate solution equivalent to 25 ml. of standard bromate solution, and
C = milliliters of sodium thiosulfate solution required in the titration.

(*e*) **Blank Determination.**—A blank determination shall be made, using the same procedure as outlined above, and using approximately the same amounts of reagents. The titration results shall be corrected accordingly.

NOTES.—1. An excess of the 8-hydroxyquinoline reagent should be used. If it is small, the result of the determination of magnesia may be low; on the other hand, if large, the result may be high. The following guide may be used:

Approximate Content of Magnesia, %	Approximate Amount of Reagent Required, ml.
0 to 1.5	10
1.5 to 3.0	15
3.0 to 4.5	20
4.5 to 6.0	25

2. The precipitate should be filtered within an hour. Prolonged standing may cause high result.

3. The amount of the standard bromate solution used may be as follows:

Approximate Content of Magnesia, %	Amount of Standard Bromate Solution, ml.
0 to 1	10
1 to 2	15
2 to 3	20
3 to 4	25
4 to 5	30
5 to 6	35

PHOSPHORUS

Special Solutions Required: 5. (*a*) ***Ammonium Molybdate.***—Dissolve 100 g. of molybdic acid (85% MoO_3) in a mixture of 400 ml. of water and 100 ml. of NH_4OH (sp.gr. 0.90) and cool the solution to room temperature. While stirring constantly, pour this solution very slowly into a cooled mixture of 500 ml. of water and 400 ml. of HNO_3 (sp.gr. 1.42). No permanent precipitate should form, which does not redissolve with stirring. Add 1 drop of a saturated solution of sodium-ammonium phosphate ($NaNH_4HPO_4$) to the solution, shake it thoroughly, and allow it to stand at least 24 hr. before use. Filter portions of the solution as needed.

(*b*) ***Magnesia Mixture.***—Dissolve 50 g. of $MgCl_2 \cdot 6H_2O$ and 100 g. of NH_4Cl in 500 ml. of water. Make the solution slightly alkaline with NH_4OH and allow it to stand at least 12 hr. Filter the solution, acidify it with HCl and dilute to 1 liter.

Procedure. 6. (*a*) Weigh a 1 to 3-g. sample of cement (Note) into a 250-ml. beaker. Treat the cement with 50 to 75 ml. of water and then with 10 to 15 ml.

of HNO_3 (sp.gr. 1.42). Boil the mixture until the solution is as complete as possible. If the cement contains an appreciable amount of manganese as shown by the presence of a red or brown residue, add a few milliliters of a potassium nitrite solution (5%) to aid in the solution. Boil the solution until all nitrous fumes are completely expelled, taking care not to allow the volume of the solution to become so small as to cause the precipitation of gelatinous silica. Filter the solution into a 500-ml. Erlenmeyer flask and wash the residue. The volume of the solution should now be about 150 ml.

NOTE.—The amount of sample and reagents used depend on the content of phosphorus in the cement. The minimum requirements are sufficient if the cement contains 0.5% P_2O_5 or more. The maximum amounts are required if the content of P_2O_5 is 0.1% or less.

(*b*) Add 10 g. of ammonium nitrate to the solution and heat until the salt is dissolved. Heat the solution to 85° C. and add 50 to 100 ml. of the solution of ammonium molybdate. Stopper the flask and shake it vigorously for 5 min., then set it aside for 30 min. Filter the precipitate, rinsing the flask five times and washing the filter paper eight times with a cold solution of potassium nitrate (1%).

(*c*) Put the original flask under the funnel containing the precipitate. Pour 25 ml. of diluted NH_4OH (1 : 4) over the precipitate and around the upper edges of the filter paper until the precipitate is entirely dissolved. Wash the paper three times with cold water, twice with diluted HCl (1 : 1), and finally three times with cold water. Acidify the solution with HCl and add to it 4 or 5 drops of a saturated solution of citric acid to hold traces of iron, if any, in solution. Cool the solution to room temperature and transfer it to a 400-ml. beaker. The volume of the solution should now be about 150 ml.

(*d*) To the solution add 25 ml. of magnesia mixture, and then while stirring constantly add drop by drop 50 ml. of NH_4OH (sp.gr. 0.90) at such a rate that 5 min. are required for the addition. Allow the mixture to stand 4 hr. or longer. Filter the precipitate and wash it a few times with diluted NH_4OH (1 : 20). Dissolve the precipitate into the original beaker by pouring 25 ml. of diluted HCl (1 : 1) on the precipitate. Wash the filter paper thoroughly with diluted HCl (1 : 20). With the washings and water, dilute the solution to 50 to 100 ml. and add to it 1 to 2 ml. of magnesia mixture. While stirring constantly, add NH_4OH slowly to the solution as before. Allow the mixture to stand 2 hr. or longer. Filter the precipitate, scrub and rinse the beaker, and wash the precipitate ten times with diluted NH_4OH (1 : 20). Ignite the precipitate in a weighed crucible at 1100° to 1200° C. to constant weight. Multiply the weight of the magnesium pyrophosphate ($Mg_2P_2O_7$) by 0.6379 to get the weight of the phosphorus in the sample as P_2O_5.

(*e*) **Blank Correction.**—Make a blank determination, using the same procedure as outlined above, and using approximately the same amount of reagents. Correct the weight of magnesium pyrophosphate ($Mg_2P_2O_7$) accordingly.

(*f*) If a determination of phosphorus is required, the weight of the ferric oxide and alumina ($Al_2O_3+Fe_2O_3$) as obtained by the method described in Section 12 of the Standard Methods of Sampling and Testing Portland Cement (A. S. T. M. Designation: C 77) of the American Society for Testing Materials shall be corrected for the amount of the P_2O_5 found.

Manganese

Special Solutions Required: 7. (*a*) ***Standard Sodium Arsenite Solution.***—Dissolve in 100 ml. of water 3.0 g. of Na_2CO_3 and then 0.9008 g. of As_2O_3, heating the mixture until the solution is as complete as possible. If the solution is not clear or contains a residue, filter the solution. Cool it to room temperature, transfer it to a volumetric flask, and dilute it to 1 liter. Each milliliter of this solution is approximately equivalent to 0.003 g. of Mn_2O_3.

(*b*) Dissolve 0.58 g. of $KMnO_4$ in 1 liter of water and standardize it against 0.0300 g. of sodium oxalate oxidimetric standard furnished by the National Bureau of Standards (Standard Sample No. 40) according to the directions furnished with the sodium oxalate. Put 30.0 ml. of the $KMnO_4$ solution in a 250-ml. Erlenmeyer flask. Add 60 ml. of diluted HNO_3 (1 : 4) and 10 ml. of a potassium nitrite solution (5%) to the flask. Boil the solution until the nitrous acid is completely expelled. Cool the solution and add sodium bismuthate and finish by titrating with the standard solution of As_2O_3 in the manner described below for the determination of manganese of cement.

(*c*) The value of the standard solution of As_2O_3 in terms of Mn_2O_3 is:

$$\frac{0.03 \times 0.236 \times 30}{a \times b},$$

where a = the number of milliliters of the solution of $KMnO_4$ required by 0.0300 g. of $Na_2C_2O_4$, and

b = the number of milliliters of the standard solution of As_2O_3 required by 30.0 ml. of the solution of $KMnO_4$.

Procedure.—8. (*a*) Weigh a 1.0 to 3.0-g. sample of cement (Note 1) into a 250-ml. beaker and treat it with 5 to 10 ml. of water and then with 60 to 75 ml. of diluted HNO_3 (1 : 4). Boil the mixture until the solution is as complete as possible. Add 10 ml. of a sodium nitrite solution (5%) to the solution and boil it until the nitrous acid is completely expelled (Note 2), taking care not to allow the volume of the solution to become so small as to cause the precipitation of a gelatinous silica. There may be some separated silica which may be ignored; but if there is still a red or brown residue, use more solution of sodium nitrite to effect a complete decomposition and then boil again to expel the nitrous acid. Filter the solution into a 250-ml. Erlenmeyer flask and wash the filter paper with water.

Notes.—1. The amount of cement taken for analysis depends on the content of manganese, varying from 1 g. for about 1% of Mn_2O_3 to 3 g. for 0.25% or less of Mn_2O_3.

2. When sodium nitrite is added, the expulsion of nitrous acid by boiling must be complete. If any nitrous acid remains in the solution, it will react with the added sodium bismuthate and decrease its oxidizing value. If there is any manganese in the cement, the first small quantity of sodium bismuthate should bring out a purple color.

(*b*) The solution should have a volume of 100 to 125 ml. Cool it to room temperature. To the solution add a total of 0.5 g. of sodium bismuthate in small quantities, with intermittent shaking. After the addition is completed, shake the solution occasionally for 5 min. and then add to it 50 ml. of cool diluted HNO_3 (1 : 33) which has been previously boiled to expel nitrous acid. Filter the solution through a pad of ignited asbestos in a Gooch crucible or a carbon filter with the aid of suction. Wash the residue four times with the cool

diluted HNO_3 (1 : 33). Titrate the filtrate immediately with the standard solution of As_2O_3. The endpoint is reached when a yellow color is obtained free of brown or purple tints and it does not change upon further addition of As_2O_3. Calculate the manganese in the cement as Mn_2O_3.

(*c*) **Blank Correction.**—Make a blank determination, using the same procedure as outlined above and using approximately the same amounts of reagents. Correct the titration results accordingly.

(*d*) If a determination of manganese is required in addition to a determination of magnesium by Section 16 of Standard Method C 77, manganese shall be eliminated from the combined filtrates obtained in the alumina and ferric oxide determination before calcium oxide is precipitated (Section 15 of Standard Method C 77) in the following manner:

Acidify the combined filtrates with HCl and evaporate them to a volume of about 100 ml. Add 40 ml. of saturated bromine water to the hot solution and immediately add NH_4OH until the solution is distinctly alkaline. Boil the solution for 5 min. or more, making certain that the solution is at all times distinctly alkaline. Allow the precipitate to settle, filter and wash with hot water. Discard the precipitate. Acidify the filtrate with HCl and boil until all the bromine is expelled. Make the solution alkaline with NH_4OH and proceed in accordance with Section 15 of Standard Method C 77.

J. LAWRENCE SMITH'S METHOD FOR ALKALIES

For the determination of total alkalies in hydraulic cement or clinker, weigh 5 grams of the finely pulverized sample and mix with 1 gram NH_4Cl by grinding the two together in an agate mortar. Add 4 grams C.P. calcium carbonate and continue the grinding until a thorough mixture has been secured. Place about ¼ inch of C.P. calcium carbonate in the bottom of a large fusion crucible, and then add the above mixture. Cover with about ¼ inch of C.P. calcium carbonate.

Mount the crucible through a hole in an asbestos board about ⅛ inch thick, so that about ¼ inch of the crucible projects above the board. Cover the crucible with a well-fitting cover and set a platinum crucible containing some water on the cover. This serves to keep the cover cool, so as to prevent loss of alkali by volatilization, and water should be kept in the crucible through the entire ignition period. Heat the crucible at a very low temperature at first, and gradually raise the temperature to a full Bunsen flame. This gradual heating should require about 1 hour, and at no time should the heating be strong enough so that the NH_4Cl fumes can be seen issuing from the crucible. Finally heat for a full hour at the full flame of the Bunsen burner.

Remove the fusion with hot water and transfer to a 375 ml. casserole. Allow to digest for several hours with about 150 ml. of hot water. If possible,

this digestion should be carried on over night. Then boil the solution for a minute, allow to settle and pour the clear liquid through a 12.5 cm. paper into a 600-ml. beaker. If there are any lumps in the casserole, grind them with an agate pestle, add about 50 ml. water, and boil for a few minutes. Allow to settle, decant the clear liquid through the same paper, add 30 ml. water and bring to boiling temperature, allow to settle and decant the clear liquid through the same paper. Repeat this washing by decantation three times and finally wash the residue into the filter. Rinse the casserole thoroughly and wash the residue in filter once with hot water.

Evaporate the filtrate to about 50 ml., add a few grams of solid ammonium carbonate and boil for a minute. Filter through an 11 cm. paper into a 250-ml. beaker, washing six times with cold water containing a little concentrated ammonia and about 10 gms. ammonium carbonate per liter. To the filtrate add 10 ml. saturated ammonium oxalate solution and 5 ml. 1–1 ammonia water and evaporate down to about 10 to 20 ml. Filter through a 9 cm. paper into a platinum dish, washing five times with hot water. Add 2 or 3 ml. concentrated HCl to the solution in the dish, and evaporated to dryness.

Ignite the residue in the dish cautiously over a free flame until the fumes of ammonium salts are driven off and finally heat at a temperature short of dull redness. Cool the dish, take up the residue in about 50 ml. of hot water, add 1.5 ml. 10% $BaCl_2$ solution. Digest on water bath for about 30 minutes, filter, and wash 5 times with hot water. Evaporate the filtrate to about 50 ml. Add 2 or 3 grams solid ammonium carbonate, boil for a minute, filter, and wash with ammonia-carbonate wash water.

To the filtrate add half a gram solid ammonium carbonate, 2 ml. saturated ammonium oxalate solution and a few ml. or 1–1 ammonia water. Evaporate the solution down to about 10 ml. and filter through a 9 cm. paper into a clean platinum dish, washing 5 times with hot water. Add 1 ml. concentrated HCl and evaporate to dryness. Heat at a temperature short of dull redness until all ammonium salts are driven off, cool in a dessicator, and weigh. After weighing, dissolve the salts in about 50 ml. hot water, and filter through a 9 cm. paper into a 150 ml. beaker. Wash the paper 5 times with hot water, and then place it in the platinum dish. Ignite until the paper is consumed, cool, and weigh. The difference between these two weights gives the weight of the alkalies as sodium and potassium chlorides.

To the solution in the 150-ml. beaker add a few ml. of 1–1 HCl and evaporate to 10 ml. Then add 6 ml. of platinum solution containing 5 g. $H_2PtCl_6 \cdot 6H_2O$ per 100 ml. for every 0.10 gms. of mixed chlorides weighed, and 3 ml. in excess. Evaporate on a water bath to a thick syrup. Carry this evaporation as far as possible without allowing the solution to go to dryness. The syrupy solution should solidify on cooling. Then add about 100 ml. of 85% ethyl alcohol, stirring the solution thoroughly. The potash in the sample will now be precipitated as yellow potassium platinic chloride, while the sodium is in solution.

Allow the precipitate to settle and filter the clear liquid through a weighed Gooch crucible. Wash the precipitate in the beaker 5 times by decantation with 80% ethyl alcohol. Transfer the precipitate to the crucible with the alcohol and scrub the beaker. Wash the crucible and precipitate 6 times with

the alcohol. Dry the crucible for several hours at 105° C., cool, and weigh as potassium platinic chloride (K_2PtCl_6).

Calculate the K_2O and Na_2O in the sample as follows:

$$\text{Weight } K_2PtCl_6 \times 0.1938 = \text{weight } K_2O,$$
$$\text{Weight } K_2PtCl_6 \times 0.3067 = \text{weight KCl},$$
$$\text{Weight mixed chlorides} - \text{weight KCl} = \text{weight NaCl},$$
$$\text{Weight NaCl} \times 0.5303 = \text{weight } Na_2O.$$

Make a blank determination, using the same procedure as outlined above and using approximately the same amounts of reagents and correct the determination of alkalies accordingly.

RAPID METHOD FOR CHEMICAL ANALYSIS OF PORTLAND CEMENT

Before submitting the cement to a chemical analysis it should be passed through a No. 50 test sieve to free it from pieces of clinker too large to be quickly decomposed by acid.

Silica.[13]—Weigh 0.5 gram of cement into a tall form 200-ml. beaker, add 12 to 15 ml. of 60% perchloric acid and cover with a watch glass. Boil the mixture until the dense white fumes in the beaker clear up and the acid refluxes down the sides of the beaker for about ten minutes. Take care not to allow the mixture to evaporate to dryness as it may not be possible to free the silica from dehydrated impurities. Take care not to allow hot concentrated perchloric acid to come in contact with organic matter as such a contact may result in an explosion. Allow the mixture to cool to room temperature. Wash the watch glass and the sides of the beaker with hot water increasing the volume of the mixture to about 50 ml. and add 5 ml. hydrochloric acid, specific gravity 1.19. Boil the mixture for one or two minutes. Filter the residue and wash it, twice with hot dilute hydrochloric acid (1 : 20) and then with hot water. Reserve the filtrate for the determination of ferric oxide and alumina. Ignite the residue in a tared platinum crucible, at first slowly with lid on until the paper is well charred, then more strongly until the residue is white, and finally at 1000–1100° C. for 45 minutes. Weigh as SiO_2.

Ferric Oxide and Alumina.—Follow the A. S. T. M. Standard Method C 77, page 1602.

Calcium Oxide.—To the filtrate (volume 300 to 400 ml.) add 2 or 3 ml. ammonium hydroxide, specific gravity 0.90. Put in a rubber-tipped stirring rod to prevent bumping. Bring the solution to a boil and, keeping the boiling up, add slowly 25 ml. of a boiling 5% solution of ammonium oxalate. Continue

[13] See also "A Rapid Method for the Determination of Silica in Portland Cement," Earl E. Maczkowski, J. of Res. of the National Bur. of Standards, **16**, No. 6, June 1936.

the boiling for 5 to 10 minutes and then allow the mixture to stand for 15 to 20 minutes. Filter, receiving the filtrate in a 600-ml. beaker. Wash the precipitated calcium oxalate eight or ten times with hot water. Reserve the filtrate and washings for the determination of magnesia. Wash the precipitate back into the original beaker. Add about 250 ml. of hot water and 20 ml. of sulfuric acid (1 : 1). Heat the solution just short of boiling and titrate it with standard potassium permanganate solution, adding the filter paper when the titration is nearly completed. Calculate the per cent of CaO in the sample.

Potassium Permanganate Solution.—Make up the solution on the basis of 5.634 grams to one liter and standardize it with National Bureau of Standards Standard Sample of Sodium Oxalate or with high grade sodium oxalate specially made by chemical manufacturers for this purpose. The latter is more economical but should be checked with a sample from the National Bureau of Standards. Dissolve 0.7500 gram of sodium oxalate in 250 ml. of hot water and add 20 ml. of sulfuric acid (1 : 1). Heat the solution just short of boiling and titrate it with the permanganate solution. If the reading is 62.8 ml., the standard solution is exactly of the required strength and a reading in analysis gives directly the percentage of calcium oxide in a half gram sample. If the reading in standardization is not 62.8, it is more satisfactory to use a table of corrections than to attempt to adjust the strength of the solution because the solution deteriorates rapidly and forms a sediment of manganese dioxide. The percentage of calcium oxide is equal to $62.8a \div s$ where a is the reading in analysis and s is the reading in standardization.

Magnesia.—Acidify the filtrate with hydrochloric acid and boil it down to about 250 ml. When the solution is cooled to room temperature, add 30 ml. 5% solution of sodium ammonium phosphate and 30 ml. of concentrated ammonia water. Stir the mixture vigorously until a crystalline precipitate is formed. Stand the mixture several hours, preferably overnight. Filter the precipitate and wash it with 5% ammonia water. Ignite it in a tared crucible, at first slowly until the paper is burned off and then at 1000–1100° C. for 30 to 45 minutes. Weigh as $Mg_2P_2O_7$ and calculate the percentage of MgO in the sample.

Other Components.—Use the A. S. T. M. Standard Method C 77 and Tentative Method C 114 which may be modified in order to gain speed.[14]

NOTE.—This method in principle is similar to methods generally used by cement plant laboratories for routine work. The rapid methods give fairly accurate results and serve their purpose well, especially when they are occasionally checked against the official methods of the A. S. T. M. The use of perchloric acid for the dehydration of silica was first proposed by Willard and Cake, J. Am. Chem. Soc., **42**, 2208 (1920), and has been improved for use on cement by numerous analysts.

[14] See also: "Determination of Sulfuric Anhydride in Portland Cement by Means of the Wagner Turbidimeter," Robert B. Rudy, J. Res. National Bur. of Standards, **16**, No. 6, June 1936. "Determination of Sulfur Occurring as Sulfide in Portland Cement," Harry A. Bright, J. Res. National Bur. of Standards, **16**, No. 2, February 1937.

RAPID METHOD FOR THE DETERMINATION OF CARBONATES IN RAW MATERIALS

Weigh out 0.500 gram of very finely ground sample into a 500-ml. Erlenmeyer flask. Add 60 ml. of 0.200 N hydrochloric acid and boil for about 5 minutes, using a reflux condenser to prevent the loss of acid. Wash the condenser down and cool the flask in a stream of cold water. Add a few drops of 0.5% phenolphthalein indicator and titrate with 0.200 N sodium hydroxide solution to the first pink coloration which may be momentary. Shake the flask vigorously during the titration and add the last portion of the alkali dropwise. Add x ml. excess of sodium hydroxide. If the content of magnesium is high and the red color fades rapidly, it may be necessary to add the excess alkali in several small amounts with boiling between additions until a permanent red color is obtained. See below in regard to the required amount of x. Call the total volume of sodium hydroxide s. Transfer the contents of the flask to a 200-ml. test tube, add the rinsings, and bring the volume to 100 ml. Heat the mixture to boiling and then allow it to stand until the precipitated magnesium hydroxide settles. If the precipitate is large, it may be necessary to filter it on a dry filter paper. Draw 50 ml. of the clear solution with a pipette. Put it in the original flask and titrate with the standard hydrochloric acid to the disappearance of the red color. Call the volume of acid used in this back titration h.

On the assumption that all the calcium and magnesium in the sample exist as carbonates, values are calculated thus:

$$\% \ MgCO_3 = 1.68\ (x-2h),$$
$$\% \ CaCO_3 = 2.0\ (60+2h-s).$$

This assumption is applicable to high grade limestone but is in general not so to raw mix used in cement manufacture on account of the insoluble silicates of calcium and magnesium. In the case of raw mix the factors should be greater than 1.68 and 2.0 and may be established by an accurate determination of total magnesium and total calcium in a standard sample of raw mix. The factors may be calculated thus:

$$\text{Factor for } MgCO_3 = \frac{\text{total Mg as } MgCO_3}{x-2h},$$

$$\text{Factor for } CaCO_3 = \frac{\text{total Ca as } CaCO_3}{60+2h-s}.$$

A factor thus obtained is valid only if the raw mix in analysis is similar to the standard sample of raw mix. If the composition of raw mix varies, total magnesium and total calcium should be determined from time to time and the factors be changed accordingly.

If the content of magnesia is consistently much lower than the limit allowed by specifications, the determination of magnesium carbonate may be omitted. Stop the determination of calcium carbonate at the appearance of the first pink coloration. x and h will be zero in the formulae given above for calcium carbonate. When magnesium carbonate is determined, its content decides the

amount of excess sodium hydroxide, x, to be used. It should be so as to make h equal to 0.2 to 0.5 ml. If insufficient sodium hydroxide is used magnesium may not be completely precipitated. If too much is used, calcium may be partially precipitated with magnesium hydroxide.

NOTE.—This method has been in common use for about thirty years.

ANALYSIS OF LIMESTONE, LIME, RAW MIX, ETC.

If the ratio of lime to silica, alumina, and ferric oxide in a sample is equal to about two or greater, it is convenient to make a sinter in a 10 ml. platinum crucible at about 1300° C. for analysis. A blast lamp with illuminating gas and compressed air is good. If properly made the sinter is easy to remove from the crucible. If a little material adheres to the bottom of the crucible, it may be removed with a few drops of hydrochloric acid. The sinter may be dissolved in acid and analyzed like Portland cement.

If the ratio of lime to silica, alumina and ferric oxide is much less than two, the mixture is liable to fuse and such a fusion is very difficult to remove. To overcome this danger, it is practical to add a little chemically pure calcium carbonate to the mixture before the ignition. Its exact weight should be known only when a determination of calcium is involved.

The determination of ferric oxide may be high due to platinum dissolved from the crucible. The presence of platinum may be recognized when stannous chloride is added to reduce ferric ions. Platinum will cause the colorless solution to turn yellow in a few minutes. To eliminate platinum, first remove silica either by boiling with perchloric acid as in the method for the rapid analysis of Portland cement, or by a single evaporation in hydrochloric acid to dryness. Then precipitate ferric oxide and alumina once with ammonia and dissolve the precipitate in hydrochloric acid after it is thoroughly washed with hot water. Then follow the usual procedure, starting with stannous chloride.

This method of decomposition may also be applied to silicate rocks when only an approximate analysis is desired. It is necessary to decrease the weight of sample to about 0.2 gram and to use about one gram of pure calcium carbonate. A good sinter may also be obtained by the ignition of a mixture of 0.5 gram of sample, 0.5 gram of calcium carbonate, and 0.5 gram of sodium carbonate at about 1000° C. However, the presence of sodium is undesirable as the precipitated calcium oxalate is contaminated by occluded sodium oxalate to the extent of about 0.003 gram unless the calcium oxalate is dissolved in acid and re-precipitated. For quick work the calcium is precipitated once and corrected for both the addition of pure calcium carbonate and the occluded sodium oxalate, the approximate amount of which is known from experiments.

NOTE.—This method has been in common use for about thirty years.

DETERMINATION OF FREE LIME IN CEMENT

Revised Procedure.[15]—The determination is based on the solution of the uncombined lime in a hot solution of glycerol and alcohol and the subsequent titration of the dissolved lime with an alcoholic solution of ammonium acetate in accordance with the reaction

$$CaO+2CH_3COONH_4=(CH_3COO)_2Ca+H_2O+2NH_3.$$

Prepare a solution consisting of 1 part by volume of U. S. P. glycerol and 5 parts by volume of absolute ethyl alcohol or anhydrous alcohol denatured in accordance with Formula 3-a or Formula 2-b of the Bureau of Internal Revenue. To each liter of this solution add 2 ml. of an indicator prepared by dissolving 1 gram of phenolphthalein in 100 ml. of absolute alcohol. It is essential that the glycerol-alcohol solution be neutral to the indicator. If the solution is colorless, add a dilute alcoholic solution of sodium or potassium hydroxide until the pink color appears, and just remove this by a drop of an alcoholic solution of ammonium acetate. If the initial color is pink, just remove it by the alcoholic solution of ammonium acetate.

A standard alcoholic solution of ammonium acetate, approximately 0.2 N, is required. Dissolve 16 grams of crystalline ammonium acetate in 1 liter of absolute ethyl alcohol or anhydrous alcohol denatured by Formula 3-a or Formula 2-b. Standardize this solution by titrating against pure calcium oxide. The calcium oxide should be freshly prepared by calcining pure calcite or calcium oxalate in a platinum crucible at 900° to 1000° C. to constant weight. Ordinary C.P. CaO should not be used. Pulverize a few grams of the calcite or calcium oxalate to an impalpable powder and heat as before. Weigh about 0.1 gram and transfer to a 200-ml. Erlenmeyer flask containing 60 ml. of the neutralized glycerol-alcohol solution. Disperse the calcium oxide in the solution by shaking. Insert a water or air reflux condenser in the neck of the flask, and boil the mixture for 20 minutes. Then remove the condenser and immediately titrate the solution, while near boiling, with the ammonium acetate solution. Replace the condenser and boil the solution again for 20 minutes. Repeat the titrations at 20-minute intervals. The titration is complete when no further color appears in the solution during continuous boiling for 1 hour. Then calculate the value of the solution in terms of grams of lime equivalent to each milliliter of ammonium acetate solution.

Grind the cement to be tested to an impalpable powder. Weigh a 1-gram sample and transfer it to a 200-ml. Erlenmeyer flask containing 60 ml. of the glycerol-alcohol solution. Shake the flask to disperse the cement in the solution. Attach the reflux condenser and boil the mixture on the hot plate. Titrate, as in the standardization, at 20-minute intervals, until no further color appears after boiling for an hour. In the final titrations, if there is doubt of the exact end point, add a drop of indicator to the quiescent liquid in the flask, carefully observing the point at which the indicator strikes the solution. If no color appears the end point has been reached. Then calculate the uncombined lime content of the cement from the known lime value of the ammonium acetate solution used.

NOTE.[16]—The determination of free lime in fresh clinker is generally made at a Portland cement plant for the control of the burning process. A large amount of free

[15] Method of W. Lerch and R. H. Bogue, Ind. Eng. Chem., Anal. Ed., 2, 296 (1930); Paper No. 23 of the Portland Cement Association at the National Bureau of Standards.

[16] By W. C. Hanna.

lime renders cement unsound. Less value is attached to the method when applied to aged cement because the method does not differentiate between calcium oxide and calcium hydroxide. The latter results from the reaction of calcium oxide and calcium silicates and aluminates with atmospheric water and has no harmful effect on the properties of cement.

EXAMPLES OF CEMENT

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
SiO_2	17 to 27	21.16	22.61	20.08	20.54	26.66	24.66	28.91
Al_2O_3	3 to 10	5.65	5.30	6.54	4.75	2.86	5.60	10.96
Fe_2O_3	0 to 7	2.23	5.23	2.40	6.05	1.76	0.38	4.68
CaO	57 to 70	63.36	59.26	65.80	61.50	64.10	61.87	34.64
MgO	0 to 5	4.20	3.55	1.40	3.89	1.27	0.90	14.82
SO_3	1 to 2.5	1.61	1.81	2.50	1.54	1.43	1.51	1.04
Loss on ignition	0.5 to 4	0.97	1.21	1.12	0.70	1.60	3.84	4.50
Insoluble residue	0 to 1	0.09	0.09	0.12	0.09	0.11		

A. Extremes for Portland cement, from cement literature.

B. Standard Portland cement for general use, manufactured in California. Average of results by ten analysts, reported by the Working Committee on Methods of Chemical Analysis, Committee C-1, A. S. T. M.

C. Low heat Portland cement for mass concrete, manufactured in California for use by the City of Pasadena, California, in Morris Dam. Average of results by ten analysts, reported by the Working Committee on Method of Chemical Analysis, Committee C-1, A. S. T. M.

D. High early strength Portland cement for rapid hardening, manufactured in California. Analysis by O. D. Guire, Jr., California Portland Cement Co., Colton, California.

E and *F*. Sulfate-resisting Portland cement for resistance to corrosion by sulfate water, manufactured in California. Analysis by O. D. Guire, Jr., California Portland Cement Company, Colton, California.

G. White Portland cement manufactured in Pennsylvania. Analysis given in Meade's "Portland Cement."

H. Natural cement manufactured in Rosendale District, New York. Analysis by C. Richardson, quoted in Eckel's "Cements, Limes and Plasters."

EXAMPLES OF CEMENT RAW MATERIALS

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
SiO_2	55.52	65.86	8.55	91.28	0.74	0.54	17.04	1.74	15.37
Al_2O_3	14.98	9.05	3.08	2.74	0.25	0.11	6.90	0.90	9.13
Fe_2O_3	5.48	3.69	78.67	0.40	0.09	0.07	2.13	0.28	0.25
CaO	7.30	6.35	4.63	2.10	55.65	32.60	37.53	49.84	25.50
MgO	3.85	2.52	1.08	0.45	0.85	1.54	2.17	1.75	12.35
SO_3	0.78					43.29		1.12	
Loss on ignition	6.22	8.32	3.82	2.39	42.40	21.94	32.88	46.01	35.40

A. Clay found in California.

B. Shale found in California.

C. Iron ore found in Mojave Desert, California.

D. Sand found in Nevada.

E. Limestone found in California.

F. Gypsum found in California.

Analyses *A* to *F*, inclusive, by O. D. Guire, Jr., California Portland Cement Co., Colton, California.

G. Cement rock found in Lehigh Valley, Pennsylvania.

H. Marl found in Indiana. Analysis by S. B. Newberry.

I. Natural-cement rock found in Rosendal District, New York. Analysis by L. C. Beck.

Analyses *G*, *H*, and *I* given in Eckel's "Cements, Limes and Plasters."

STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COAL AND COKE

STANDARD METHOD OF SAMPLING COAL [1]

A. S. T. M. Designation: D 21–16 [2]

It is imperative that every sample be collected and prepared carefully and conscientiously and in strict accordance with the standard methods described herein, for if the sampling is improperly done, the sample will be in error, and it may be impossible or impracticable to take another sample; but if an analysis is in error, another analysis can easily be made of the original sample.

Gross samples of the quantities designated herein must be taken whether the coal to be sampled consists of a few tons or several hundred tons, because of the following cardinal principle in sampling coal that must be recognized and understood; that is, the effect of the chance inclusion or exclusion of too many or too few pieces of slate or other impurities in what, or from what, would otherwise have been a representative sample will cause the analysis to be in error accordingly, regardless of the tonnage sampled. For example, the chance inclusion or exclusion of 10 lb. too much or too little of impurities in or from an otherwise representative sample of 100 lb. would cause the analysis to show an error of approximately 10 in ash percentage, and in heat units of approximately 10%, whereas for a 1000-lb. sample, the error would be approximately one tenth as large, being the same whether the sample is collected from a 1-ton lot or from a lot consisting of several hundred tons.

When this method of sampling is to be employed as a part of any contract or agreement, the following provisions shall be specifically agreed to by the parties to such contract or agreement:

(*a*) The place at which the coal is to be sampled.
(*b*) The approximate size of the sample required when the standard conditions do not apply.
(*c*) The number of samples to be taken or the amount of coal to be represented by each sample when the standard conditions do not apply.

FOR ALL DETERMINATIONS EXCEPT TOTAL MOISTURE

Time of Sampling.—The coal shall be sampled when it is being loaded into or unloaded from railroad cars, ships, barges, or wagons, or when discharged

[1] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-5 on Coal and Coke. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[2] This method is issued under the fixed designation D 21; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1915; Adopted, 1916. This method has been approved as American Tentative Standard by the American Standards Association.

from supply bins, or from industrial railway cars, or grab buckets, or from any coal-conveying equipment, as the case may be. If the coal is crushed as received, samples usually can be taken advantageously after the coal has passed through the crusher. Samples collected from the surface of coal in piles or bins, or in cars, ships or barges are generally unreliable.

Size of Increments.—To collect samples, a shovel or specially designed tool, or mechanical means shall be used for taking equal portions or increments. For slack or small sizes of anthracite, increments as small as 5 to 10 lb. may be taken, but for run-of-mine or lump coal, increments should be at least 10 to 30 lb.

Collection of Gross Sample.—The increments shall be regularly and systematically collected, so that the entire quantity of coal sampled will be represented proportionately in the gross sample, and with such frequency that a gross sample of the required amount shall be collected. The standard gross sample shall not be less than 1000 lb., except that for slack coal and small sizes of anthracite in which the impurities do not exist in abnormal quantities or in pieces larger than ¾ in., a gross sample of approximately 500 lb. shall be considered sufficient. If the coal contains an unusual amount of impurities, such as slate, and if the pieces of such impurities are very large, a gross sample of 1500 lb. or more shall be collected. The gross sample should contain the same proportion of lump coal, fine coal, and impurities as is contained in the coal sampled. When coal is extremely lumpy, it is best to break a proportional amount of the lumps before taking the various increments of a sample. Provision should be made for the preservation of the integrity of the sample.

Quantity Represented.—A gross sample shall be taken for each 500 tons or fraction thereof, or in case of larger tonnages, for such quantities as may be agreed upon.

Crushing.—After the gross sample has been collected, it shall be systematically crushed, mixed, and reduced in quantity to convenient size for transmission to the laboratory. The sample may be crushed by hand or by any mechanical means, but under such conditions as shall prevent loss of coal or the accidental admixture of foreign matter. Samples of the quantities indicated in Table I shall be crushed so that no pieces of coal and impurities will be greater in any dimension, as judged by eye, than specified for the sample before division into two approximately equal parts.

The method of reducing by hand the quantity of coal in a gross sample shall be carried out as prescribed in Section 6, even should the initial size of coal and impurities be less than indicated in Table I.

TABLE I

Weight of Sample to be Divided, lb.	Largest Size of Coal and Impurities Allowable in Sample before Division, in.
1000 or over	1
500	¾
250	½
125	⅜
60	¼
30	$\frac{3}{16}$ or to pass a 4760-micron (No. 4) sieve

FIRST STAGE IN THE PREPARATION OF A 1,000-POUND SAMPLE
1
Crush 1,000-pound sample on hard, clean surface to 1″ size
2
1,000-pound sample crushed to 1″ and coned
3
Mix by forming long pile
A - spreading out first shovelful.
B - long pile completed
4
Halving by alternate shovel method. Shovelfuls 1,3,5, etc., reserved as 5, A; 2,4,6 etc., rejected as 5, B
5
Long pile divided into two parts
A - reserve; B - reject
NOTE:
SELECT A HARD, CLEAN SURFACE, FREE OF CRACKS AND PROTECTED FROM RAIN, SNOW, WIND, AND BEATING SUN. DO NOT LET CINDERS, SAND, CHIPPINGS FROM FLOOR, OR ANY OTHER FOREIGN MATTER GET INTO THE SAMPLE PROTECT SAMPLE FROM LOSS OR GAIN IN MOISTURE.
SECOND STAGE
6
Crush 500-pound sample (fig.5, A) to ¾″ size
7
500 pounds crushed to ¾″ and coned
8
Mix by forming long pile
A - spreading out first shovelful.
B - long pile completed
9
Halving by alternate shovel method. Shovelfuls 1,3,5, etc., reserved as 10, A; 2,4,6 etc., rejected as 10, B
10
Long pile divided into two parts;
A - reserve; B - reject
THIRD STAGE
11
Crush 250-pound sample (fig.10: A) to ½″ size
12
250-pounds crushed to ½″ and coned
13
Mix by forming new cone
14
Quarter after flattening cone
15
Sample divided into quarters
16
Retain opposite quarters A, A,
Reject quarters B, B
FOURTH STAGE
17
Crush 125-pound sample (fig.16: A, A) on blanket to ⅜″ size
18
Mix by rolling on blanket
19
Form cone after mixing
20
Quarter after flattening cone
21
Sample divided into quarters
22
Retain opposite quarters A, A,
Reject quarters B, B
FIFTH STAGE
23
Crush 60-pound sample (fig.22: A, A) to ¼″ size
24
Mix by rolling on blanket
25
Form cone after mixing
26
Quarter after flattening cone
27
Sample divided into quarters
28
Retain opposite quarters A, A,
Reject quarters B, B
SIXTH STAGE
29
Crush 30 pound sample (fig.28: A, A) to 3/16″ or to pass a 4760-micron (No.4) Sieve
30
Mix by rolling on blanket
31
Form cone after mixing
32
Quarter after flattening cone
33
Sample divided into quarters
34
The laboratory sample to be taken from A, A

FIG. 225.—Standard Methods of Sampling Coal.

Hand Preparation.—The progressive reduction in the weight of the sample to the quantities indicated in Table I shall be done by the following methods, which are illustrated in Fig. 225;

(*a*) **Mixing and Reduction by Discarding Alternate Shovelfuls.**—The alternate-shovel method of reducing the gross sample shall be repeated until the sample is reduced to approximately 250 lb., and care shall be observed before each reduction in quantity that the sample has been crushed to the fineness prescribed in Table I.

The crushed coal shall be shoveled into a conical pile (Fig. 225) by depositing each shovelful of coal on top of the preceding one, and then formed into a long pile in the following manner: The sampler shall take a shovelful of coal from the conical pile and spread it out in a straight line (Fig. 3A or 8A) having a width equal to the width of the shovel and a length of 5 to 10 ft. The next shovelful shall be spread directly over the top of the first shovelful, but in the opposite direction, and so on back and forth, the pile being occasionally flattened, until all the coal has been formed into one long pile (Fig. 225, 4 or 9). The sampler shall then discard half of this pile, proceeding as follows:

Beginning on one side of the pile, at either end, and shoveling from the bottom of the pile, the sampler shall take one shovelful (shovelful No. 1, Fig. 3B or 8B) and set it aside; advancing along the side of the pile a distance equal to the width of the shovel, he shall take a second shovelful (shovelful No. 2) and discard it; again advancing in the same direction one shovel width, he shall take a third shovelful (shovelful No. 3) and add it to the first. The fourth (shovelful No. 4) shall be taken in a like manner and discarded, the fifth (shovelful No. 5) retained, and so on, the sampler advancing always in the same direction around the pile so that its size will be gradually reduced in a uniform manner. When the pile is removed, about half of the original quantity of coal should be contained in the new pile formed by the alternate shovelfuls which have been retained. (Fig. 5A or 10A show the retained halves, and Fig. 5B or 10B the rejected halves.)

(*b*) **Mixing and Reduction by Quartering.**—After the gross sample has been reduced by the alternate-shovel method to approximately 250 lb., further reduction in quantity shall be by the quartering method. Before each quartering, the sample shall be crushed to the fineness specified in Table I.

Quantities of 125 to 250 lb. shall be mixed thoroughly by coning and reconing (Figs. 12 and 13); quantities less than 125 lb. shall be placed on a suitable cloth, measuring about 6 by 8 ft., mixed by raising first one end of the cloth and then the other (Fig. 18, 24 or 30), so as to roll the coal back and forth, and after being mixed thoroughly shall be formed into a conical pile by gathering together the four corners of the cloth (Fig. 19, 25 or 31). The quartering of the conical pile shall be done as follows:

The cone shall be flattened, its apex being pressed down vertically with a shovel, or board, so that after the pile has been quartered, each quarter will contain the material originally in it. The flattened mass, which shall be of uniform thickness and diameter, shall then be marked into quarters (Fig. 14, 20, 26 or 32) by two lines that intersect at right angles directly under a point corresponding to the apex of the original cone. The diagonally opposite quarters (*BB* in Fig. 16, 22, 28 or 34) shall then be shoveled away and

discarded and the space that they occupied brushed clean. The coal remaining shall be crushed, mixed, coned, and quartered successively until the sample is reduced to the desired quantity.

(*c*) The 30-lb. quantity (Fig. 29) shall be crushed to $\frac{3}{16}$-in. size or to pass a 4760-micron (No. 4) sieve, mixed, coned, flattened and quartered. The laboratory samples shall include all of one of the quarters, or all of two opposite quarters (Fig. 34), as may be required. The laboratory sample shall be placed immediately in a suitable container and sealed in such a manner as to preclude tampering.

Mechanical Preparation.—Only such mechanical means as will give equally representative samples shall be used in substitution for the hand method of preparation herein standardized.

FOR THE DETERMINATION OF TOTAL MOISTURE

Collection of Moisture Sample.—The special moisture sample shall weigh approximately 100 lb., and shall be accumulated by placing in a waterproof receptacle with a tight-fitting and waterproof lid small equal parts of freshly taken increments of the standard gross sample. The accumulated moisture sample shall be rapidly crushed and reduced mechanically or by hand to about a 5-lb. quantity, which shall be immediately placed in a container and sealed air-tight and forwarded to the laboratory without delay.

Use of Standard Sample.—Only when equally representative results will be obtained shall the standard gross sample be used instead of the special moisture sample for the determination of total moisture.

STANDARD METHOD OF SAMPLING COKE FOR ANALYSIS [3]

A. S. T. M. Designation: D 346–35 [4]

It is imperative that every sample be collected and prepared carefully and conscientiously and in strict accordance with the standard procedure described herein, for if the sampling is improperly done, the sample will be in error, and it may be impossible or impracticable to take another sample; whereas if an analysis is in error, another analysis can readily be made of the original sample.

[3] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-5 on Coal and Coke. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St. Philadelphia, Pa.

[4] This method is issued under the fixed designation D 346; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1932; Adopted in Amended Form, 1935.

Gross samples of not less than the quantities designated herein must be taken whether the coke to be sampled consists of a few tons or several hundred tons in order to minimize the effect of the chance inclusion or exclusion of too many or too few pieces of non-representative material.

FOR ALL DETERMINATIONS EXCEPT TOTAL MOISTURE

Time of Sampling.—(*a*) The coke shall be sampled while it is being loaded into or unloaded from railroad cars, ships, barges, or trucks, or when discharged from supply bins, railroad cars, grab buckets, or other coke-conveying equipment.

(*b*) Samples collected from the surface of coke in piles, bins, cars, ships or barges are, in general, unreliable because of size segregation and should not be used for determining conformance to specifications unless the purchaser and seller so agree. In case it is necessary to collect a sample of coke from the surface of loaded shipments, nine equal increments shall be taken about 1 ft. below the surface. The nine sampling points shall be located as shown in Fig. 226.

Size of Increments.—To collect samples, a shovel or specially designed tool or mechanical means shall be used for taking equal portions or increments. The gross sample shall consist of not less than 25 nor more than 50 increments of approximately equal quantity, except that when samples are collected from the surface of loaded shipments the gross sample shall consist of 9 increments of approximately equal quantity.

Collection of Gross Sample.—The increments shall be regularly and systematically collected, so that the entire quantity of coke sampled will be represented proportionately in the gross sample, and with such frequency that a gross sample of the required amount will be collected. The standard gross sample shall be not less than the quantities given in the following table:

Minimum Weights of Gross Samples of Coke

Run-of-oven, Blast-furnace, Foundry, Water-gas, and any coke containing a range of size of pieces made from uncrushed or coarsely crushed coal,[b] except coke breeze	500 lb.[a]
Run-of-oven, Blast-furnace, Foundry, Water-gas, and any coke containing a range of size of pieces made from crushed coal,[c] except coke breeze	250 lb.[a]
Closely-sized coke made from uncrushed or coarsely crushed coal [b] free of coke breeze	250 lb.[a]
Closely-sized coke made from crushed coal [c] free of coke breeze	125 lb.[a]
Coke breeze (all passing a ½ or ¾-in. square-hole sieve)	125 lb.

[a] In case the pulverization of the coal is not known, take quantities designated for coke made from uncrushed or coarsely crushed coal.

[b] More than 10% on a ¼-in. square-hole sieve.

[c] Not less than 90% passing through a ¼-in. square-hole sieve.

Quantity Represented.—A gross sample shall be taken for each 250 tons or fraction thereof, or in case of larger tonnages, for such quantities as may be agreed upon. Each lot of coke arising from a different source or known to be of different quality or size shall be sampled separately.

Crushing.—The entire gross sample shall be crushed, mixed, and reduced in quantity to convenient size for transmission to the laboratory. The sample

shall be crushed preferably by means of jaw or roll crushers, or in case mechanical crushing means are not available, the coke sample shall be crushed on a chilled-iron or hard-steel plate by impact of a tamper, hard bar or sledge, avoiding all rubbing action, as otherwise the ash content may be materially increased by the addition of iron from the sampling apparatus, even though hardened iron or steel is used. The crushing shall be done under such conditions as shall

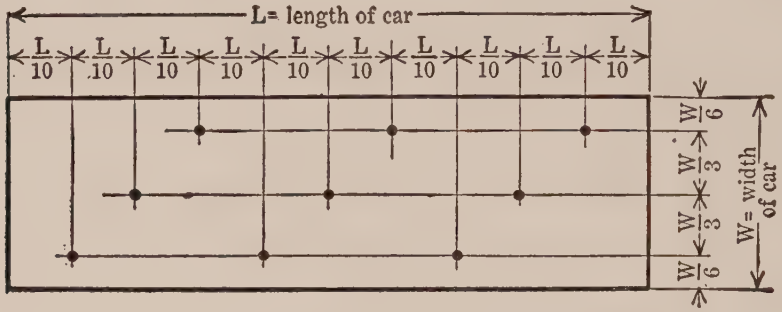


Fig. 226.—Location of Sampling Points from Exposed Surface of Car.

prevent loss of coke or accidental admixture of foreign matter. Samples of the quantities indicated in Table I shall be crushed so that no pieces of coke and impurities will be greater in dimension, as judged by eye, than specified for the sample before division into two approximately equal parts.

Table I.—Weights of Coke Samples with Corresponding Crushing Sizes.

Weight of Sample to be Divided, lb.	Largest Size of Coke and Impurities Allowable in Sample Before Division
250 or over	1 in.
125	¾ in.
60	½ in.
30	¼ in.

The method of reducing by hand the quantity of coke in a gross sample shall be carried out as described in Section 6, even should the initial size of coke and impurities be less than indicated in Table I.

Mixing and Reduction.—The progressive reduction in the weight of the sample to the quantities indicated in Table I shall be done by the following methods which are described and illustrated in Plate V of the Standard Method of Sampling Coal (A. S. T. M. Designation: D 21) of the American Society for Testing Materials.[5]

(*a*) The alternate-shovel method of reducing the gross sample shall be repeated until the sample is reduced to approximately 125 lb., and care shall be observed before each reduction in quantity that the sample has been crushed to the fineness specified in Table I.

The crushed coke shall be shoveled into a conical pile (Fig. 225, 2 or 7) [5] by depositing each shovelful of coke on top of the preceding one, and then

[5] Page 1622.

formed into a long pile in the following manner: The sampler shall take a shovelful of coke from the conical pile and spread it out in a straight line (Fig. 3*A* or 8*A*) having a width equal to the width of the shovel and a length of 5 to 10 ft. The next shovelful shall be spread directly over the top of the first shovelful, but in the opposite direction, and so on back and forth, the pile being occasionally flattened, until all the coke has been formed into one long pile (Fig. 3*B* or 8*B*). The sampler shall then discard half of this pile, proceeding as follows:

Beginning on one side of the pile, at either end, and shoveling from the bottom of the pile, the sampler shall take one shovelful (shovelful No. 1, Fig. 4 or 9) and set it aside; advancing along the side of the pile a distance equal to the width of the shovel, he shall take a second shovelful (shovelful No. 2) and discard it; again advancing in the same direction one shovel width, he shall take a third shovelful (shovelful No. 3) and add it to the first. The fourth (shovelful No. 4) shall be taken in a like manner and discarded, the fifth (shovelful No. 5) retained, and so on, the sampler advancing always in the same direction around the pile so that its size will be gradually reduced in a uniform manner. When the pile is removed, about half of the original quantity of coke should be contained in the new pile formed by the alternate shovelfuls which have been retained. (Fig. 5*A* or 10*A* show the retained halves, and Fig. 5*B* or 10*B* the rejected halves.)

(*b*) After the gross sample has been reduced by the alternate-shovel method to approximately 125 lb., further reduction in quantity shall be by the quartering method. Before each quartering, the sample shall be crushed to the fineness specified in Table I.

Quantities of 60 to 125 lb. shall be mixed thoroughly by coning and reconing (Figs. 12 and 13); quantities less than 60 lb. shall be placed on a suitable cloth, measuring about 6 by 8 ft., mixed by raising first one end of the cloth and then the other (Fig. 18, 24 or 30), so as to roll the coke back and forth, and after being mixed thoroughly shall be formed into a conical pile by gathering together the four corners of the cloth (Fig. 19, 25 or 31). The quartering of the conical pile shall be done as follows:

The cone shall be flattened, its apex being pressed down and worked outward by means of a shovel, so that after the pile has been quartered, each quarter will contain the material originally in it. The flattened mass, which shall be of uniform thickness and diameter, shall then be marked into quarters (Fig. 14, 20, 26 or 32) by two lines that intersect at right angles directly under a point corresponding to the apex of the original cone. The diagonally opposite quarters (*BB* in Fig. 16, 22, 28 or 34) shall then be shoveled away and discarded and the space that they occupied brushed clean. The coke remaining shall be crushed, mixed, coned, and quartered successively until the sample is reduced to approximately 30 lb.

(*c*) The 30-lb. quantity shall be crushed to ¼-in. size, mixed, coned, flattened and quartered. The laboratory samples shall include all of one of the quarters, or all of the two opposite quarters, as may be required. The laboratory sample shall be placed immediately in a suitable container and sealed in such a manner as to preclude tampering.

Reduction by Mechanical Means.—Only such riffles or other mechanical means as will give equally representative samples shall be used in substitution for the hand method of reduction in quantity herein standardized.

For the Determination of Total Moisture

Sample for Total Moisture.—For determining total moisture, a special moisture sample weighing approximately 50 lb. shall be taken, except in the case of coke breeze, in which case the moisture sample shall weigh approximately 25 lb. The moisture sample shall be taken when the coke is being loaded or unloaded as the case may be, and shall be accumulated by placing in a waterproof receptacle with a tight-fitting lid small equal parts of the freshly-taken increments of the standard gross sample as previously described. The special moisture sample, without any preliminary crushing, shall preferably be dried to constant weight at a temperature of not less than 104 nor more than 200° C.[6] In case it is impracticable to dry the entire sample, the following procedures may be used:

For Coke Appearing Dry.—The special moisture sample shall be crushed rapidly to ½-in. size and reduced mechanically or by hand to about a 5-lb. quantity, which shall be immediately placed in a container and sealed air-tight and forwarded to the laboratory without delay.

For Coke Appearing Wet.—The special moisture sample shall be spread on tared pans, weighed, and air-dried or dried in a warm place or on a warm or heated surface until the coke appears dry, and weighed again. The sampling shall be completed as described in the preceding paragraph for coke appearing dry. This loss in weight divided by weight of sample, multiplied by 100, is the percentage of air-drying loss and should be corrected as follows for the moisture found in the sample sent to the laboratory:

$$\text{Percentage total moisture (as received)} = \frac{100 - \text{percentage of air-drying loss}}{100} \times \text{percentage moisture in air-dried sample} + \text{percentage of air-drying loss.}$$

Report.—Since in the report of the analysis, a brief description should be given of the method of taking the sample, by such characteristic expressions as "Belt Sample," "Top-of-car," etc., information as to how the sample is taken shall be included in the description which accompanies the sample sent to the laboratory.

[6] Experiments made at the U. S. Bureau of Mines have shown that results checking within 0.5% are obtained between these temperature limits. See A. C. Fieldner and W. A. Selvig, "The Determination of Moisture in Coke," U. S. Bureau of Mines Technical Paper No. 148 (1917).

STANDARD METHODS OF LABORATORY SAMPLING AND ANALYSIS OF COAL AND COKE[7]

A. S. T. M. Designation: D 271–33;[8]

PREPARATION OF LABORATORY SAMPLES

Apparatus: (*A*) ***For Coal:*** The apparatus used for sampling coal shall consist of the following:

(*a*) ***Air Drying Oven.***—An oven for air-drying wet samples. A suggested form is shown in Fig. 227. Such an oven is not essential but is economical where many samples are to be dried.[9]

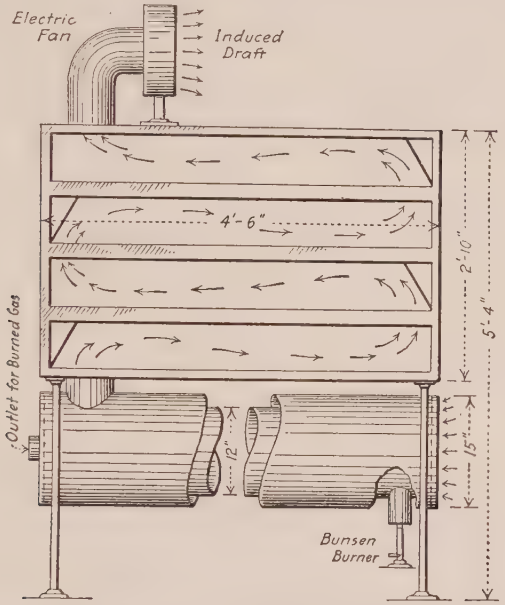


Fig. 227.—Drier for Coarse Samples. The outlet for air at the top may be connected with a chimney or any other device which will furnish a suitable draft. (*Bulletin No. 9*, Geological Survey of Ohio, p. 312.)

[7] Under the standardization procedure of the Society, these methods are under the jurisdiction of the A. S. T. M. Committee D-5 on Coal and Coke.

These methods comprise a revision and combination of the former Standard Methods of Laboratory Sampling and Analysis of Coal (A. S. T. M. Designation: D 22–24) and of Laboratory Sampling and Analysis of Coke (A. S. T. M. Designation: D 37–24) which methods were accordingly discontinued in 1927.

[8] These methods are issued under the fixed designation D 271; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Adopted, 1916, 1918; Revised, 1921, 1924, 1927, 1929, 1930, 1933. These methods have been approved as American Standard by the American Standards Association.

[9] For details of air-drying oven, see F. M. Stanton and A. C. Fieldner and W. A. Selvig, "Methods of Analyzing Coal and Coke," U. S. Bureau of Mines Technical Paper No. 8, p. 2 (1929). Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St. Philadelphia, Pa.

(*b*) ***Pans for Air-Drying Wet Samples.***—Galvanized iron pans 18 by 18 in. by 1.5 in. in depth.

(*c*) ***Balance or Solution Scale.***—A balance or scale having a capacity of 5 kg. sensitive to 0.5 g. for weighing the galvanized iron pans with samples.

(*d*) ***Crusher.***—A jaw crusher suitable for crushing coarse samples to pass a 4760-micron (No. 4) sieve.

(*e*) ***Grinder.***—A roll crusher or coffee-mill type of grinder suitable for reducing the material passing a 4760-micron (No. 4) sieve to pass an 840-micron (No. 20) sieve. To reduce the moisture loss while crushing, a coffee-mill type of grinder should be entirely enclosed and have an enclosed hopper and receptacle capable of holding 10 lb. of coal.

(*f*) ***Pulverizer.***—An Abbé ball mill, planetary disk crusher, chrome-steel bucking board, or any satisfactory form of pulverizer for reducing the material passing an 840-micron (No. 20) sieve to pass a 250-micron (No. 60) sieve. The porcelain jars for the ball mill should be approximately 9 in. in diameter and 10 in. high. The flint pebbles should be smooth, hard and well rounded.

(*g*) ***Large Riffle Sampler.***—A large riffle sampler with ½ or ⅝-in. divisions for reducing the coal passing the 4760-micron (No. 4) sieve to 10 lb. (see Fig. 228).

(*h*) ***Small Riffle Sampler.***—A small riffle sampler with ¼ or ⅜-in. divisions for reducing the material passing the 840-micron (No. 20) and the 250-micron (No. 60) sieves to a laboratory sample (see Fig. 229).

(*i*) ***Sieve.***—An 8-in. 250-micron (No. 60) sieve with cover and receiver.

NOTE.—The sieve designations employed are those of the Standard Specifications for Sieves for Testing Purposes (A. S. T. M. Designation: E 11) of the American Society for Testing Materials,[10] and all sieves shall conform to the detailed requirements of these specifications. See p. 1329.

(*j*) ***Containers.***—Samples in which the moisture content is important should always be shipped in moisture-tight containers. A galvanized-iron or tin can with an air-tight friction top or a screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit. Samples in which the moisture content is of no importance need no special protection from loss of moisture.

(*B*) ***For Coke:*** The apparatus used for sampling coke shall consist of the following:

(*a*) ***Pans for Total Moisture Determination.***—Galvanized iron pans 24 by 24 in. by 4 in. in depth.

(*b*) ***Balance or Solution Scale.***—A balance or scale having a capacity of 10 kg. sensitive to 1 g. for weighing the galvanized-iron pans with samples.

(*c*) ***Crusher.***—As described under Section A.

(*d*) ***Roll-Crusher.***—A hard-steel roll crusher suitable for reducing the material passing a 4760-micron (No. 4) sieve to pass an 840-micron (No. 20) sieve.

(*e*) ***Pulverizer.***—An Abbé ball mill, hard-steel roll crusher or hard-steel diamond mortar for reducing the product passing an 840-micron (No. 20) sieve to pass a 250-micron (No. 60) sieve. The porcelain jars for the ball mill

[10] 1933 Book of A. S. T. M. Standards, Part II, p. 1244.

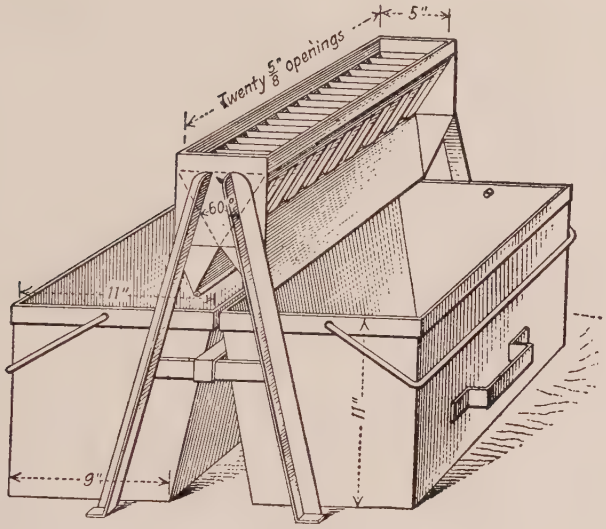


FIG. 228.—Large Riffle Sampler.

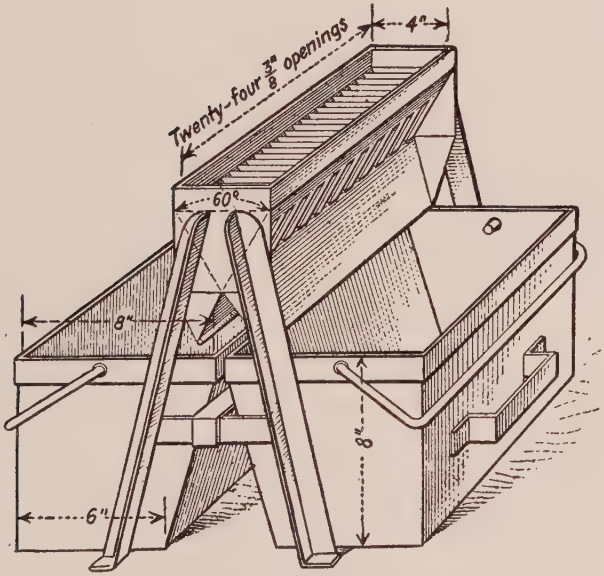


FIG. 229.—Small Riffle Sampler.

should be approximately 9 in. in diameter and 10 in. high. The flint pebbles should be smooth, hard and well rounded. The rolls of the hard-steel roll crusher should revolve at the same speed.

(*f*) ***Large Riffle Sampler.***—Same as in Section A (*g*) for reducing coke passing the 4760-micron (No. 4) sieve to 10 lb. (see Fig. 228).

(*g*) ***Small Riffle Sampler.***—The same as Section A (*h*) (see Fig. 229).

(*h*) ***Sieve.***—The same as Section A (*i*).

(*i*) ***Containers.***—The same as Section A (*j*).

(*j*) ***Oven, Stove or Hot Plate.***—An oven, stove or hot plate for drying coke samples in the determination of total moisture. If an oven is used it should have openings provided for natural ventilation and should be capable of being regulated between 104 and 200° C. If the coke is dried on a stove or hot plate a thermometer should be placed in it, and care exercised that the temperature does not exceed 200° C. at any point in the pan of coke.

Method of Sampling: (*A*) ***For Coal Appearing Dry:*** (*a*) If the sample is coarser than will pass completely a 4760-micron (No. 4) sieve and larger in amount than 10 lb., quickly crush it with the jaw crusher to pass a 4760-micron (No. 4) sieve and reduce it on the larger riffle sampler to 10 lb.;[11] then crush it at once to pass an 840-micron (No. 20) sieve by passing through rolls or an enclosed grinder, and take, without sieving, a 50-g. total moisture sample, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the product passing an 840-micron (No. 20) sieve, and should be placed directly in a rubber-stoppered bottle.

(*b*) Thoroughly mix the main portion of the sample, reduce on the small riffle sampler to about 200 g., and pulverize to pass a 250-micron (No. 60) sieve by any suitable apparatus without regard to loss of moisture. After all the material has been passed through the 250-micron (No. 60) sieve, mix and divide it on the small riffle sampler to about 50 g. Transfer the final sample to a 4-oz. rubber-stoppered bottle. Determine moisture in both the 250-micron (No. 60) sieve sample and the 840-micron (No. 20) sieve sample in accordance with Sections 6, 7, and 8 under the Determination of Moisture.

(*c*) ***Calculation.***—Calculate the analysis of the coal passing the 250-micron (No. 60) sieve which has become partly air-dried during sampling, to the dry-coal basis, by dividing each result by 1 minus its content of moisture. Compute the analysis of the coal "as received" from the dry-coal analysis by multiplying by 1 minus the total moisture found in the sample passing an 840-micron (No. 20) sieve.

(*B*) ***For Coal Appearing Wet:*** (*a*) Spread the sample on tared pans, weigh, and air-dry at room temperature, or in the special drying oven, shown in Fig. 227, at 10 to 15° C. above room temperature, and weigh again. The drying should be continued until the loss in weight is not more than 0.1% per hour. Complete the sampling as described in Section 3 for dry coal.

(*b*) ***Calculation.***—Correct the moisture found in the air-dried sample passing an 840-micron (No. 20) sieve to total moisture "as received," as follows:

[11] If the sample is crushed to pass a 3360-micron (No. 6) sieve it may be reduced to 5 lb.

$\frac{100 - \text{percentage of air-drying loss}}{100} \times$ (percentage of moisture in air-dried sample passing an 840-micron (No. 20) sieve) + (percentage of air-drying loss) = (total moisture "as received")

(*c*) Calculate the analysis to "dry-coal" and "as-received" bases as described in Section 3 for dry coal, using for the "as-received" calculation the total moisture as found by the formula in Paragraph (*b*) in place of the moisture found in the coal passing an 840-micron (No. 20) sieve.

NOTES.—Freshly mined or wet coal loses moisture rapidly on exposure to the air of the laboratory, hence the sampling operations between opening the container and taking the total-moisture sample passing an 840-micron (No. 20) sieve must be conducted with the utmost dispatch and with minimum exposure to air.

The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ more than the following limits:

No carbonates present	0.4%
Considerable carbonate and pyrite present	0.7%
Coals with more than 12% ash, containing considerable carbonate and pyrite	1.0%

(*C*) ***Ball-mill Method for Coal Appearing Wet or Dry:*** (*a*) This method of sampling [12] does not require a total moisture sample of the coal passing an 840-micron (No. 20) sieve as do methods *A* and *B*. The coal is first air-dried to bring it to a condition of approximate equilibrium with the air to minimize moisture change during the preparation of the sample for analysis. After air-drying all operations are performed with the utmost dispatch to prevent moisture change. Fine grinding of the sample is done in an air-tight ball mill. Total moisture is computed from the air-drying loss and the residual moisture in the sample prepared for analysis.

(*b*) Spread the sample on tared pans, weigh, and air-dry in the special mositure oven shown in Fig. 227, at 10 to 15° C. above room temperature until the loss in weight between two successive weighings, made 6 to 12 hours apart, does not exceed 0.1% per hour. Record the loss in weight as "air-drying loss."

(*c*) Immediately after the last weighing, quickly crush the entire sample by means of a roll-crusher adjusted so the product will pass an 840-micron (No. 20) sieve. Then, without sieving, quickly reduce the coal on the small riffle sampler to about 200 g. Put this 200-g. portion at once in the porcelain jar (1-gal. capacity) of an Abbé ball mill, sealed air-tight by means of a rubber gasket, and grind to pass a 250-micron (No. 60) sieve. The jar shall be slightly more than half full of well-rounded flint pebbles, about ¾ in. in diameter, and rotated at 60 to 75 r.p.m. Bituminous coals require from 10 to 20 minutes and anthracite about 1 hour of rotation to be pulverized to the designated fineness.

(*d*) When pulverization is complete, pour the contents of the jar on a ½-in. square-mesh sieve, and separate the sample from the pebbles by shaking the sieve over a rubber mixing-cloth. Brush carefully the pebbles and inside of the jar to remove any adhering pulverized coal. A convenient size of sieve is one approximately 17 in. square. Then quickly pass the sample through a

[12] This method of sampling is used by the U. S. Bureau of Mines, see F. M. Stanton, A. C. Fieldner and W. A. Selvig, "Methods of Analyzing Coal and Coke." U. S. Bureau of Mines Technical Paper No. 8, p. 2 (1929).

250-micron (No. 60) sieve. To minimize moisture change, keep the sieve covered while the sample is being sieved. Usually some coarse particles, amounting to 0.2 to 0.4% of the sample, remain on the sieve. As these particles are likely to consist largely of ash-forming substances, reduce them on a chromium-steel bucking board to pass the sieve and then add to what passed through the sieve. Quickly mix the sample on a rubber mixing-cloth and reduce to about 50 g. by passing through the small riffle sampler. Put this 50-g. portion which constitutes the laboratory sample, in a rubber-stoppered, wide-mouth, 4-oz. bottle. To minimize moisture change, the mixing and reducing of the pulverized sample after removal from the ball mill shall be done with utmost dispatch. The total time elapsing from the opening of the porcelain jar to the stoppering of the laboratory sample shall not exceed 3 minutes.

Calculation.—As all the analytical determinations are made on the air-dried sample passing a 250-micron (No. 60) sieve, calculate the analysis to "as-received" and "dry-coal" bases from the analysis of the air-dried coal in the following manner:

CALCULATION FROM ANALYSIS OF "AIR-DRIED" COAL TO COAL "AS RECEIVED"

All figures expressed in per cent

$$\text{Moisture "as received"} = \text{moisture} \times \frac{(100 - \text{air-drying loss})}{100} + \text{air-drying loss.}$$

$$\text{Volatile matter "as received"} = \text{volatile matter} \times \frac{(100 - \text{air-drying loss})}{100}.$$

$$\text{Fixed carbon "as received"} = \text{fixed carbon} \times \frac{(100 - \text{air-drying loss})}{100}.$$

$$\text{Ash "as received"} = \text{ash} \times \frac{(100 - \text{air-drying loss})}{100}.$$

$$\text{Sulfur "as received"} = \text{sulfur} \times \frac{(100 - \text{air-drying loss})}{100}.$$

$$\text{Hydrogen "as received"} = \text{hydrogen} \times \frac{(100 - \text{air-drying loss})}{100} + 1/9 \text{ air-drying loss.}$$

$$\text{Carbon "as received"} = \text{carbon} \times \frac{(100 - \text{air-drying loss})}{100}.$$

$$\text{Nitrogen "as received"} = \text{nitrogen} \times \frac{(100 - \text{air-drying loss})}{100}.$$

$$\text{Oxygen "as received"} = \text{oxygen} \times \frac{(100 - \text{air-drying loss})}{100} + 8/9 \text{ air-drying loss.}$$

$$\text{Calories "as received"} = \text{calories} \times \frac{(100 - \text{air-drying loss})}{100}.$$

CALCULATION FROM ANALYSIS OF "AIR-DRIED" COAL TO "DRY COAL"

All figures expressed in per cent

$$\text{Volatile matter in "dry coal"} = \text{volatile matter} \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Fixed carbon in "dry coal"} = \text{fixed carbon} \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Ash in "dry coal"} = \text{ash} \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Sulfur in "dry coal"} = \text{sulfur} \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Hydrogen in "dry coal"} = (\text{hydrogen} - 1/9\ \text{moisture}) \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Carbon in "dry coal"} = \text{carbon} \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Nitrogen in "dry coal"} = \text{nitrogen} \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Oxygen in "dry coal"} = (\text{oxygen} - 8/9\ \text{moisture}) \times \frac{100}{100 - \text{moisture}}.$$

$$\text{Calories in "dry coal"} = \text{calories} \times \frac{100}{100 - \text{moisture}}.$$

(*D*) ***For Coke:*** (*a*) ***Total Moisture Determination.***—Dry the entire sample received at the laboratory, without any preliminary crushing, to constant weight at a temperature of not less than 104 nor more than 200° C.[13]

Calculate the loss in weight to percentage of moisture, which shall constitute the total moisture in the coke as received at the laboratory.

The allowable difference in duplicate determinations by the same analyst is 0.5%.

(*b*) ***Reduction of Sample.***—Crush the dried sample mechanically with a jaw or roll crusher, or by hand on a chilled iron or hard-steel plate by impact of a hard bar or sledge, avoiding all rubbing action, as otherwise the ash content will be materially increased by the addition of iron from the sampling apparatus, even though hardened iron or steel is used. Continue the crushing until all the sample passes through a 4760-micron (No. 4) sieve, mix and reduce on the large riffle sampler to not less than 5 lb.; again crush the 5-lb. sample sufficiently fine to pass an 840-micron (No. 20) sieve; mix and reduce on the small riffle sampler to 200 g. Transfer this 200-g. portion to the porcelain jar of an Abbé ball mill and pulverize to pass a 250-micron (No. 60) sieve. When pulverization is complete, pour the contents of the jar on a ½-in. screen and separate the sample from the pebbles by shaking the screen. Pass all the material through a 250-micron (No. 60) sieve, pulverizing any coarse particles by impact in a hard-steel diamond mortar, and mix with the remainder of the sample. Reduce the sample through the small riffle sampler to about 50 g. and transfer to a rubber-stoppered glass bottle.

(*c*) In case a ball mill is not available for fine grinding, quarter the 5-lb. sample passing an 840-micron (No. 20) sieve to 200 g. and pulverize to pass a 250-micron (No. 60) sieve by means of a hard steel roll crusher in which the rolls revolve at the same speed, or by impact in a hard-steel diamond mortar. The use of rubbing surfaces such as a disk pulverizer or a bucking board is never permissible for grinding coke.

[13] Experiments made at the U. S. Bureau of Mines have shown that results checking within 0.5% are obtained between these temperature limits. See A. C. Fieldner and W. A. Selvig, "The Determination of Moisture in Coke," U. S. Bureau of Mines Technical Paper No. 148 (1917).

NOTE.—The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ more than 0.4%.

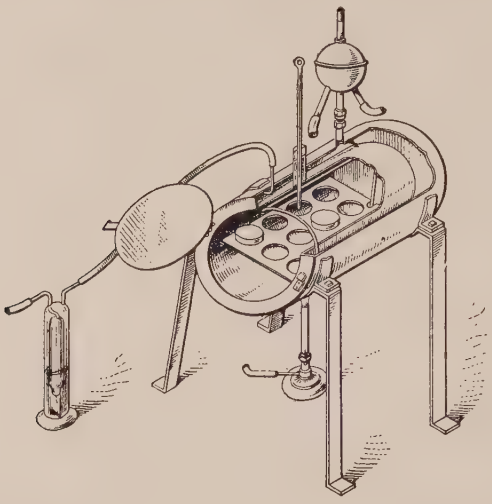


FIG. 230.—Toluene or Glycerin and Water Oven for Determining Moisture (Technical Paper No. 8, Bureau of Mines, p. 9 (1929)).

METHODS OF ANALYSIS

DETERMINATION OF MOISTURE

(For Coal and Coke)

Apparatus: (*a*) ***Moisture Oven*** (***For Coal***).—For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts and a minimum of air space. It may be of the form shown in Fig. 230. Provision shall be made for renewing the air in the oven at the rate of two to four times a minute, with the air dried by passing it through concentrated H_2SO_4.

(***For Coke***).—For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104 and 110° C. may be used.

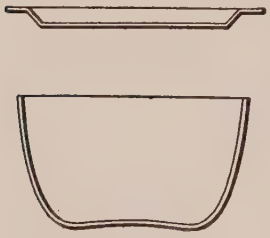


FIG. 231.—Capsule for Use in Determining Moisture.

(*b*) ***Capsules with Covers.***—A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule, $\frac{7}{8}$ in. deep and $1\frac{3}{4}$ in. in diameter; or a fused silica capsule of similar shape. This shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 231.

Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

Method: (*A*) ***For Coal or Coke Passing 250-micron (No. 60) Sieve:*** (*a*) Heat the empty capsules under the conditions at which the sample is to be dried, place stopper or cover on capsule, cool over concentrated H_2SO_4 (sp.gr. 1.84) for 30 minutes, and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g. of the sample; put this quickly into the capsule, close, and weigh at once.

(*b*) An alternate procedure (more open to error), after transferring an amount slightly in excess of 1 g., is to bring to exactly 1 g. in weight (±0.5 mg.) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used in order to minimize the exposure of the sample until the weight is found.

After removing the covers, quickly place the capsules in a preheated oven (at 104 to 110° C.) through which passes a current of air dried by concentrated H_2SO_4 (the current of dry air is not necessary for coke). Close the oven at once and heat for 1 hour. Then open the oven, cover the capsules quickly and place them in a desiccator over concentrated H_2SO_4. When cool, weigh.

The percentage of moisture in the sample passing a 250-micron (No. 60) sieve shall be used to calculate the other results to a dry basis.

(*B*) ***For Coal Passing 840-micron (No. 20) Sieve:*** Use 5-g. samples, weighed with an accuracy of 2 mg., and heat for 1½ hours; the procedure is otherwise the same as with the sample passing a 250-micron (No. 60) sieve as described in Section 8.

NOTE.—For methods of greater accuracy see Report of Subcommittee II on Moisture, of the Joint Committee on Analysis of Coal, Proceedings, Am. Soc. Testing Mats., Vol. XIV, Part I, pp. 419–423 (1914).

DETERMINATION OF ASH

(For Coal and Coke)

Apparatus: (*a*) ***Gas or Electric Muffle Furnace (for Coal).***—For determination of ash of coal, the muffle shall have good air circulation and be capable of having its temperature regulated between 700 and 750° C.

(*b*) ***Gas or Electric Muffle Furnace or Meker Burner (for Coke).***—For determination of ash of coke, the muffle shall have good air circulation and be capable of having its temperature regulated to not exceed 950° C.

(*c*) ***Porcelain Capsules.***—Porcelain capsules, ⅞ in. deep and 1¾ in. in diameter, or similar shallow dishes or platinum crucibles.

Method: (*A*) ***For Coal:*** Place the porcelain capsules containing the dried coal from the moisture determination in a cold muffle furnace, or on the hearth at a low temperature, and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter. Finish the ignition to constant weight (±0.001 g.) at a temperature between 700 and 750° C. Cool in a desiccator, and weigh as soon as cold.

NOTES.—Before replacing the capsules in the muffle for ignition to constant weight, the ash should be stirred with a platinum or nichrome wire. Stirring once or twice before the first weighing hastens complete ignition.

The result obtained by this method is "uncorrected" ash. For "corrected" ash see the preliminary report.[14] The actual mineral matters in the original coal are usually very different in weight and composition from the weight of the "uncorrected" ash.

[14] Report on Fixed Carbon and Ash, Proceedings, Am. Soc. Testing Mats., Vol. XIV, Part I, p 426 (1914).

(*B*) ***For Coke:*** Place the capsules containing the dried coke from the moisture determination in a muffle furnace or over a burner, and heat to redness at such a rate as to avoid mechanical loss. Finish the ignition to constant weight (±0.001 g.) at a temperature not exceeding 950° C. Cool in a desiccator and weigh.

NOTES.—Before replacing the capsules in the muffle for ignition to constant weight the ash should be stirred with a platinum or nichrome wire. Stirring once or twice before the first weighing hastens complete ignition.

Test the ash for unburned carbon, by moistening it with alcohol; any carbon remaining will show as black particles.

DETERMINATION OF VOLATILE MATTER

(*For Coal and Coke*)

Apparatus: (*a*) ***Platinum Crucible with Closely Fitting Cover (for Coal).***—The crucible shall be of not less than 10 nor more than 20-ml. capacity; of not less than 25 nor more than 35 mm. in diameter; of not less than 30 nor more than 35 mm. in height.

(*b*) ***Platinum Crucible with Closely Fitting Cover (for Coke).***—The crucible shall be of 10-ml. capacity, with capsule cover having thin flexible sides fitting down into crucible. Or the double-crucible method may be used, in which the sample is placed in a 10 or 20-ml. platinum crucible, which is then covered with another crucible of such a size that it will fit closely to the sides of the outer crucible, and its bottom will rest ⅛ to ½ in. above the bottom of the outer crucible.

(*c*) ***Vertical Electric Tube Furnace; or a Gas or Electrically Heated Muffle Furnace (for Coal or Coke).***—The furnace may be of the form as shown in Fig. 232. It shall be regulated to maintain a temperature of 950° C. ±20° C. in the crucible, as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal or coke is bought, a Meker burner may be used.

Method: (*A*) ***For Coal and Coke, Usual Method:*** (*a*) Weigh 1 g. of the sample in a weighed platinum crucible, close with a cover, and place on platinum or nichrome-wire supports in the furnace chamber, which shall be at a temperature of 950° C. ±20° C. After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, or in the case of coke after heating 2 or 3 minutes, tap the cover lightly to more perfectly seal the crucible and thus guard against the admission of air. After heating for exactly 7 minutes, remove the crucible from the furnace and, without disturbing the cover, allow it to cool. Coke should be cooled in a desiccator. Weigh as soon as cold. The loss of weight minus moisture equals the volatile matter.

(*b*) ***Modification for Sub-Bituminous Coal, Lignite, and Peat.***—Mechanical losses are incurred on suddenly heating peat, sub-bituminous coal, and lignite; therefore, they must be subjected to a preliminary gradual heating for 5 minutes; this is best done by playing the flame of a burner upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating, transfer the crucible to the volatile-matter furnace and heat for 6 minutes at 950° C. as in the regular method described in Paragraph (*a*).

NOTES.—The cover should fit closely enough so that the carbon deposit from bituminous and lignite coals does not burn away from the under side.

Regulation of temperature to within the prescribed limits is important.

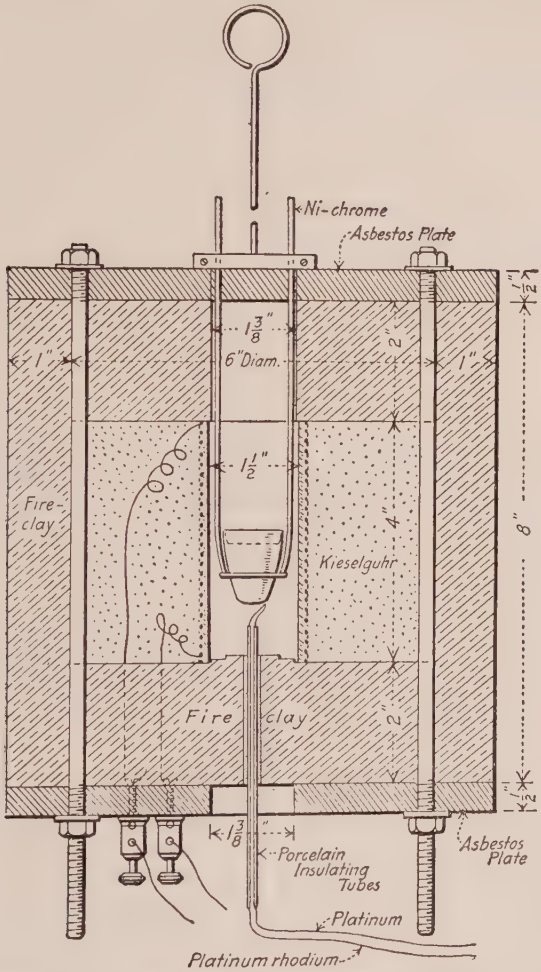


FIG. 232.—Electric Tube Furnace for Determining Volatile Matter. For 110-volt alternating current, 60 ft. of Nichrome Wire, No. 17 B. & S. gage will give the required temperature. The temperature must be controlled by an external resistance. (U. S. Bureau of Mines Technical Paper No. 8, p. 12 (1929)).

(*B*) ***For Coal and Coke, Using Meker Burner:*** Weigh 1 g. of the sample in a weighed platinum crucible and close with a cover or, in the case of coke, with another crucible. Place in the flame of a No. 4 Meker burner, having approximately an outside diameter at the top of 25 mm. and giving a flame not less than 15 cm. high. The temperature should be

950° C. ±20° C., as determined by placing a thermocouple through the perforated cover, which for this purpose may be of nickel or asbestos. The junction of the couple should be placed in contact with the center of the bottom of the crucible; or the temperature may be indicated by the fusion of pure K_2CrO_4 in the covered crucible (fusion of K_2CrO_4, 968° C.).[15] The crucible shall be placed in the flame about 1 cm. above the top of the burner and the heating continued 7 minutes. Where the gas pressure is variable it is well to use a U-tube attachment to the burner.

Determination of Fixed Carbon

(For Coal and Coke)

Calculate fixed carbon as follows:

100 − (moisture + ash + volatile matter) = percentage of fixed carbon

Determination of Sulfur

(For Coal and Coke)

A. Eschka Method

Apparatus: (*a*) ***Gas or Electric Muffle Furnace, or Burners.***—For igniting the sample with the Eschka mixture and for igniting the $BaSO_4$.

(*b*) ***Porcelain or Platinum Crucibles or Capsules.***—Porcelain capsules, 7/8 in. deep and 1¾ in. in diameter, or porcelain crucibles of 30-ml. capacity, high or low form, or platinum crucibles of similar size shall be used for igniting the sample with the Eschka mixture.

(*c*) Porcelain, platinum, alundum, or silica crucibles of 10- to 15-ml. capacity, shall be used for igniting the $BaSO_4$.

Solutions and Reagents: (*a*) ***Barium Chloride.***—Dissolve 100 g. of $BaCl_2 \cdot 2H_2O$ in 1000 ml. of distilled water.

(*b*) ***Saturated Bromine Water.***—Add an excess of bromine to 1000 ml. of distilled water.

(*c*) ***Eschka Mixture.***—Thoroughly mix two parts (by weight) of light calcined MgO and one part of anhydrous Na_2CO_3. Both materials should be as free as possible from sulfur.

(*d*) ***Methyl Orange.***—Dissolve 0.02 g. in 100 ml. of hot distilled water and filter.

(*e*) ***Hydrochloric Acid.***—Mix 500 ml. of HCl (sp.gr. 1.19), and 500 ml. of distilled water.

(*f*) ***Normal Hydrochloric Acid.***—Dilute 80 ml. of HCl (sp.gr. 1.19), to 1 liter with distilled water.

(*g*) ***Sodium Carbonate.***—A saturated solution, approximately 60 g. of crystallized or 22 g. of anhydrous Na_2CO_3 in 100 ml. of distilled water.

(*h*) ***Sodium Hydroxide Solution.***—Dissolve 100 g. in 1 liter of distilled water. This solution may be used in place of the Na_2CO_3 solution.

Method: ***Preparation of Sample and Mixture.***—Thoroughly mix on glazed paper 1 g. of the sample and 3 g. of Eschka mixture. Transfer to a porcelain capsule, 7/8 in. deep and 1¾ in. in diameter, or a porcelain crucible of 30-ml.

[15] U. S. Bureau of Mines *Reports of Investigations*, Serial No. 2917 (1929).

capacity, high or low form, or platinum crucible of similar size, and cover with about 1 g. of Eschka mixture.

(*a*) ***Ignition.***—On account of the amount of sulfur contained in artificial gas, the crucible shall be heated over an alcohol, gasoline or natural gas flame as described in Paragraph (*b*), or in a gas or electrically heated muffle, as described in Paragraph (*c*) for coal and in Paragraph (*d*) for coke. The use of artificial gas for heating the sample and Eschka mixture is permissible only when the crucibles are heated in a muffle.

(*b*) Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and stirring after all black particles have disappeared, which is an indication of the completeness of the procedure.

(*c*) (***For Coal***).—Place the crucible in a cold muffle and gradually raise the temperature to 800° C. ± 25° C. in about 1 hour. Maintain this maximum temperature for about 1½ hours.

(*d*) (***For Coke***).—Place the crucible in a warm muffle and gradually raise the temperature to 800° C. ± 25° C. in about 30 minutes. Maintain this maximum temperature until on stirring all black particles have disappeared.

(*e*) ***Subsequent Treatment.***—Remove and empty the contents into a 200-ml. beaker and digest with 100 ml. of hot water for ½ to ¾ hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 ml., with 10 to 20 ml. of saturated bromine water, make slightly acid with HCl and boil to expel the liberated bromine. Make just neutral to methyl orange with NaOH or Na_2CO_3 solution, then add 1 ml. of N HCl. Boil again and add slowly from a pipette, with constant stirring, 10 ml. of a 10% solution of $BaCl_2 \cdot 2H_2O$. Continue boiling for 15 minutes and allow to stand for at least 2 hours, or preferably over night, at a temperature just below boiling. Filter through an ashless filter paper and wash with hot distilled water until a $AgNO_3$ solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of $BaSO_4$ in a weighed platinum, porcelain, silica or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925° C. and heat to constant weight.

The residue of MgO, etc., after leaching, should be dissolved in HCl and tested with great care for sulfur. When an appreciable amount is found this should be determined quantitatively. The amount of sulfur retained is by no means a negligible quantity.[16]

(*f*) ***Blanks and Corrections.***—In all cases a correction must be applied either (1) by running a blank exactly as described above, using the same amount of all reagents that were employed in the regular determination, or more surely (2) by determining a known amount of sulfate added to a solution of the reagents

[16] Journal Am. Chemical Soc., **21**, 1125 (1899).

after these have been put through the prescribed series of operations. If this latter procedure is adopted and carried out, say, once a week or whenever a new supply of a reagent must be used, and for a series of solutions covering the range of sulfur content likely to be met with in the samples, it is only necessary to add to or subtract from the weight of $BaSO_4$ obtained from a sample, whatever deficiency or excess may have been found in the appropriate " check " in order to obtain a result that is more certain to be correct than if a " blank " correction as determined by the former procedure is applied. This is due to the fact that the solubility error for $BaSO_4$, for the amounts of sulfur in question and the conditions of precipitation prescribed, is probably the largest one to be considered. $BaSO_4$ is soluble [17] in acids and even in pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, in the event of using reagents of very superior quality or of exercising more than ordinary precautions, there may be no apparent " blank," because the solubility limit of the solution for $BaSO_4$ has not been reached or at any rate not exceeded.

(*g*) Calculate sulfur content as follows:

$$\text{Percentage of Sulfur} = \frac{(\text{Weight of } BaSO_4 - \text{blank}) \times 13.74}{\text{Weight of sample}}$$

NOTE.—As shown in the preliminary report,[18] the Atkinson and sodium-peroxide methods give results in close agreement with the Eschka method. Register [19] has shown that if 5% of nitrogen is present in the gases contained in the bomb calorimeter the sulfur of a sample is almost completely oxidized to H_2SO_4 and the washings of the calorimeter may be used for the determination of sulfur.

B. Bomb Washing Method [20]

Method: (*a*) ***Ignition.***—Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination. The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under the calorimetric determination. The bomb shall stand in the calorimeter water for not less than 5 minutes after firing.

(*b*) ***Subsequent Treatment.***—Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than one minute. Bombs equipped with valves other than needle valves, such as compression valves, shall be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases. Open the bomb and examine the inside for traces of unburned material or sooty deposit. If these are found, the determination shall be discarded. Wash carefully all parts of the interior of the bomb, including the tray, with a fine jet of distilled water containing 1 ml. per liter of a saturated solution of methyl orange, until no acid reaction is observed. It is essential to wash through the valve opening in the case of bombs equipped with compression valves, or other types of valves with large openings, as considerable spray may collect in such valve openings.

[17] Journal Am. Chemical Soc., **32**, 588 (1910); **33**, 829 (1911).
[18] Journal of Industrial and Engineering Chemistry, **5**, 5 (1913).
[19] Ibid., **6**, 812 (1914).
[20] W. A. Selvig and A. C. Fieldner, "Check Determinations of Sulfur in Coal and Coke by the Eschka, Bomb-washing, and Sodium Peroxide Fusion Methods," Industrial and Engineering Chemistry, **29**, 729–733 (1927).

Collect the washings in a 250-ml. beaker and titrate with standard alkali solution to obtain the "acid correction" for the heating value, as specified under the calorimetric determination. Add 1 ml. of NH_4OH (sp.gr. 0.90), heat the solution to boiling, and filter through qualitative filter paper. Wash the residue and filter paper thoroughly five or six times with hot distilled water. To the filtrate and washings, amounting to about 250 ml., add 1 ml. of saturated bromine water and sufficient HCl to make it slightly acid. Boil the solution to expel the excess bromine. Adjust the acidity, precipitate, and determine the sulfur as specified under the Eschka method.

C. Sodium Peroxide Fusion Method [21]

Apparatus: (*a*) ***Combustion Bomb.***—The Parr coal sulfur bomb, or its equivalent, shall be used. The bomb shall have an inner surface which is not attacked by the chemicals on ignition of the charge.

(*b*) ***Reagents.***—Sulfur-free powdered sodium peroxide (Na_2O_2), powdered c.p. potassium perchlorate ($KClO_4$) or potassium chlorate ($KClO_3$), and powdered c.p. benzoic acid shall be used.

Method: (*a*) Place 1 g. of $KClO_4$ or $KClO_3$ in a dry sulfur bomb and break up any lumps that occur. Add a 0.5-g. sample and mix thoroughly with a glass rod. Then add one measure (about 15 g.) sodium peroxide, close the bomb and mix thoroughly by shaking. In the case of cokes or anthracites, or coals excessively high in ash which fail to ignite or fuse properly (as indicated by the fusion being honey-combed in appearance), add 0.3 g. of benzoic acid to the bomb at the time the chlorate and sample are added. It should be noted that a mixture of potassium chlorate and organic matter alone produces a mixture of extremely explosive properties. One of the important functions of the sodium peroxide is to provide a diluent, thus slowing down the reaction, so care should be taken that it is not omitted in the charge. Potassium perchlorate is fully equal if not superior to the $KClO_3$, and is without turbulence in its reaction.

Fasten the cover securely to the bomb and ignite the charge by applying a sharply pointed flame from a blast lamp to the bottom of the bomb for a brief period, or by electric ignition, according to the type of bomb used. Place the bomb inside a piece of steel pipe when the charge is ignited to prevent possible injury to the operator if the bomb should burst. Allow one minute for complete combustion to take place after ignition, then cool under the tap or in a vessel of water.

Remove the cover from the bomb, place the bomb on its side in a 400-ml. beaker and wash off the cover with a fine jet of hot distilled water. Place a watch glass over the beaker and cautiously add about 100 ml. of hot distilled water. After the contents of the bomb have dissolved, remove and rinse it carefully with the distilled water. Add slowly, concentrated HCl to the neutral point, then add 1 to 2 ml. of the acid in excess. Filter through qualitative filter paper into a 600-ml. beaker and wash thoroughly five or six times with distilled water. Dilute the filtrate to approximately 400 ml. and precipi-

[21] W. A. Selvig and A. C. Fieldner, "Check Determinations of Sulfur in Coal and Coke by the Eschka, Bomb-washing, and Sodium Peroxide Fusion Methods," Industrial and Engineering Chemistry, **29**, 729–733 (1927).

tate the sulfur with barium chloride and determine as specified under the Eschka method.

(*b*) ***Blank Correction.***—A blank correction shall be applied by running a blank on the reagents used.

Determination of Phosphorus in Ash

(For Coal and Coke)

Solution Required: ***Molybdate Solution.***—Dissolve 65 g. of molybdic acid (85%) in a mixture of 143 ml. of NH_4OH (sp.gr. 0.90) and 142 ml. of water. Add this solution slowly, with constant stirring, to 715 ml. of HNO_3 (sp.gr. 1.20). If the solution is cloudy, add two drops of a solution of ammonium phosphate (20%) and allow the precipitate which forms to settle. Filter the solution into bottles and, if necessary, re-filter just before using. If the molybdic acid used is 100%, 56 g. should be taken instead of 65 g.

Method: ***Method No. 1, for all Cases:*** Add to the ash from a 5-g. sample, in a platinum crucible, 10 ml. of concentrated HNO_3 and 3 to 5 ml. of HF. Evaporate the liquid, ignite the residue, and fuse with 3 g. of Na_2CO_3. If unburned carbon is present, mix 0.2 g. of $NaNO_3$ with the carbonate. Leach the melt with water and filter the solution. Ignite the residue, fuse with Na_2CO_3 alone, leach the melt with water and filter the solution. Just acidify with HNO_3 the combined filtrate held in a flask, add 3 to 5 ml. of concentrated HNO_3 in excess, and concentrate to a volume of 100 ml. Add 6 g. of NH_4NO_3, bring the temperature of the solution to 80° C., add 50 ml. of molybdate solution and shake the flask for 10 minutes. When the precipitate has settled, filter and wash the precipitate, until free from acid, with a KNO_3 solution (2%). Place the filter paper with the precipitate in the flask, add 25 ml. of recently boiled distilled water, and macerate the filter paper with a glass stirring rod. Add a measured excess of standard NaOH solution and agitate the solution to completely dissolve the precipitate. Add 3 drops of phenolphthalein solution as an indicator and titrate the excess NaOH with a standard HNO_3 solution. The alkali solution may well be made equal to 0.00025 g. of phosphorus per milliliter, or 0.005% for a 5-g. sample. Such a solution would be 0.926 of 0.2 N.[22]

Note.—The advantage of the use of HF in the initial attack of the ash lies in the resulting removal of silica. Fusion with alkali carbonate is necessary for the elimination of titanium, which if present and not removed, will contaminate the phosphomolybdate and is said to sometimes retard its precipitation.

Method No. 2, when Titanium is Low: When titanium is so low as to offer no objection, decompose the ash as described above, ***Method No. 1,*** but carry the evaporation only to a volume of about 5 ml. Dilute the solution with water to 30 ml., boil and filter into a flask. If the washings are turbid pass them again through the filter. Ignite the residue in a platinum crucible, fuse with a little Na_2CO_3, dissolve the melt in HNO_3 and add the solution, if clear, to the main one. If not clear, filter. The fusion of the residue may be dispensed with in routine work on a given coal or coke if it is certain that the residue is free from phosphorus. Add NH_4OH until a slight precipitate ensues.

[22] Ulmann and Buch, Chemical Engineer, **10**, 130 (1909).

Add concentrated HNO_3 to just dissolve the precipitate, then add 3 to 5 ml. of the acid in excess. Heat the solution, which should have a volume of about 100 ml., to 80° C. and add 50 ml. of molybdate solution. Shake the flask for 10 minutes, filter, and determine the phosphorus as described in ***Method No. 1.***

Determination of Fusibility of Ash

(For Coal and Coke)

Apparatus: (***a***) ***Standard Furnace.***—Gas-fired furnaces such as the coal-ash fusion furnace of the Denver Fire Clay Co., the No. 3 Melter's Furnace of the American Gas Furnace Co., or their equivalent shall be used.

These gas-fired furnaces are especially suitable for fusion determination in that the burners are arranged on a tangent near the base of the furnace, thus producing a rotary flame which completely surrounds the crucible in which the ash cones are placed. The whirling flame heats the crucible uniformly and when the furnaces are operated with an excess of gas over air, a reducing atmosphere is maintained in the crucible, which condition gives the lowest point at which the ash fuses. Either natural or artificial gas may be used. Air should be supplied at uniform pressure.

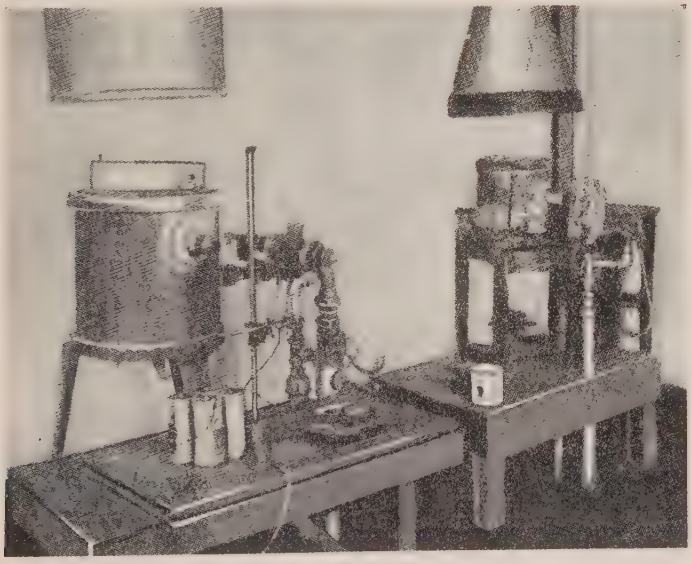


Fig. 233.—Denver Fire-Clay Furnace and No. 3 Melter's Furnace, with Accessories.

The stock design of the No. 3 Melter's Furnace should be modified by providing the upper cylinder with two holes in the side; a 2-in. observation hole with its center 4 in. from the top of the cylinder (excluding cover plate), and a 1-in. thermocouple hole 90° to the right of the observation hole; the bottoms of these holes being in the same horizontal plane. The coal-ash fusion furnace as furnished by the Denver Fire Clay Co. is provided with suitable observation

and thermocouple holes. The interior of the furnaces are cylindrical and approximately 7 in. in diameter. Counter-balanced sheet-iron canopies connected with telescopic flues to an exhaust system are placed over the furnaces for conducting the hot gases out of the room. Two furnaces and accessories are shown in Fig. 233.

(*b*) ***Refractory Crucibles.***—The interior of the fusion furnace as arranged for making a test is shown in Fig. 234. Crucible *a* is a Corundite crucible about 3 in. in inside diameter and about 4½ in. in height outside, with a wall thickness of about ½ in. The crucible is provided with a cover, *b*, and shall have two holes in the side, an observation hole 2 in. in diameter and a thermocouple hole 1 in. in diameter, 90° to the right of the observation hole. The bottoms of the two holes shall be in the same horizontal plane. The crucible is supported by a Corundite support, *c*, so that the two holes in the crucible are in line with the corresponding holes in the furnace wall. The ash cones, *d*, are supported on Corundite disk *e* so that they are visible through the observation hole of the crucible and furnace wall.

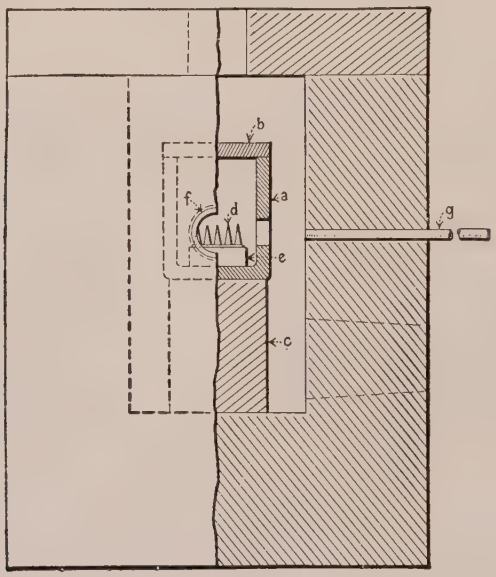


Fig. 234.—Section of Furnace Arranged for Fusion Tests.

(*c*) ***Observation Hole.***—A fused silica, alundum, or refractory porcelain tube, *f*, 1⅞ in. in external diameter and 6 to 7 in. long, is cemented in the 2 in. observation hole of the furnace, the inner end being flush with the inside furnace wall and the other end projecting out of the furnace. A brass sleeve carrying a single thin glass window, made from ordinary soda glass, shall be slipped on the outer end of the observation tube to prevent the escape of burning gas, which would interfere with a convenient observation of the cones. When observations at high temperatures are made, the cones should be viewed through a piece of colored glass.

(*d*) ***Blowing Tube.***—At furnace temperatures above 1000° C. it is very difficult to observe the ash cones. An open refractory porcelain blowing tube, *g*, Fig. 234, about ¼ in. in inside diameter shall be inserted in the thermocouple hole, the inner end being flush with the inside of the furnace wall. The blowing tube shall be connected to the compressed air line by means of rubber tubing and the air shall be let into the tube at the time of observation by means of a pinch-cock, thus momentarily cooling the ash cones and rendering them visible.

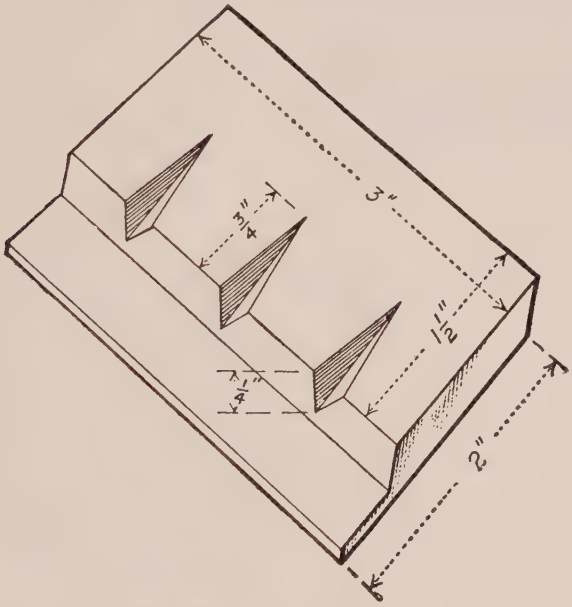


FIG. 235.—Brass Cone Mold.

(*e*) ***Brass Cone Mold.***—A brass cone mold for making ash cones, ¾ in. high and ¼ in. at each side of the base, which is an equilateral triangle, is illustrated in Fig. 235.

(*f*) ***Pyrometer.***[23]—The temperature measurements shall be made with a thermocouple of platinum and platinum-rhodium used in conjunction with a high-resistance millivoltmeter or potentiometer; or with an optical pyrometer of the disappearing filament type, which has been calibrated to be accurate to 10° C. up to 1400° C. and to 15° C. from 1400° to 1600° C. If a thermocouple is used it should be protected from the furnace gases by a glazed porcelain tube and so placed in the furnace that the hot junction is in the immediate vicinity of the cones. The pyrometer equipment shall be checked frequently by mounting small pieces of pure gold and nickel in the same manner as the cones. With a strong reducing atmosphere, 1452° C. should be obtained for the melting point of nickel and 1063° C. for the gold. The pyrometer equipment should

[23] For detailed information concerning the use of pyrometers see "Pyrometric Practice," U. S. Bureau of Standards Technologic Paper No. 170 (1921).

also be standardized from time to time through the temperature range for which it is used, by a suitably equipped standardizing laboratory, such as that of the U. S. Bureau of Standards.

(*g*) If temperature measurements are made by sighting an optical pyrometer through the glass window of the observation tube the following corrections shall be added to the observed temperatures to correct for absorption of light by the glass window:

CORRECTION TO OBSERVED TEMPERATURE FOR ABSORPTION OF LIGHT BY A SINGLE CLEAN GLASS WINDOW [24]

Observed Temperature, Deg. Cent.	Correction to be Added, Deg. Cent.
800	5
1000	8
1200	10
1400	13
1600	16

Preparation of Ash: Spread out 50 to 100 g. of the sample passing a 250-micron (No. 60) sieve on a 6-in. fire-clay roasting dish, and completely convert to ash in a muffle furnace at a temperature of 800° to 900° C. Transfer 5 to 10 g. of this ash to an agate mortar [25] and grind to pass a 74-micron (No. 200) sieve. Then place the ash in a silica or porcelain capsule, $\frac{5}{8}$ in. deep and $1\frac{3}{4}$ in. in diameter, and ignite for a period of two hours in a current of oxygen, at a temperature of 800° to 850° C. This ignition is made to insure complete and uniform oxidation of the ash.

Preparation of Cones: Moisten the ignited ash with a 10% dextrin solution and work into a plastic mass with a spatula. Mold the plastic material into small triangular pyramids $\frac{3}{4}$ in. high and $\frac{1}{4}$ in. wide at the side of the base. The pyramids are made by firmly pressing the plastic material with a steel spatula into a brass mold of the dimensions mentioned, the mold being similar to that shown in Fig. 235. Strike off the surface smooth and remove the cone from the mold by applying a small knife blade at the base. Mount the cones when dry in a refractory base composed of a mixture of equal parts of kaolin and calcined alumina. Moisten the base mixture to make it workable, and spread a part of it out on a sheet-iron plate. Then mount the cone in a vertical position in a small hole made in the base, and put base material into the hole around the bottom of the cone to fill the crevices and make the cone stand firmly. Usually five cones are mounted in one base in the manner shown in Fig. 236. Dry the sheet-iron plate with the test piece on a hot plate. Ignite the cones at a dull red heat for 30 minutes in an open muffle to remove the carbonaceous material.

Method of Heating: Place the test piece in the muffle crucible of the furnace in the position shown in Fig. 234, place the loosely fitting cover *b*, on the crucible, and ignite the gas. It is necessary to let the gas burn about 10 minutes to heat the furnace parts before the large cover plate of the furnace is replaced; otherwise the flame is apt to blow out. During this time increase the flow of

[24] U. S. Bureau of Standards Technologic Paper No. 170, p. 117 (1921).

[25] A mechanical agate-mortar grinder will save time where many determinations are made.

gas and air sufficiently to cause the combustion to take place just above the tuyeres and yet maintain a yellowish flame at least 6 in. above the opening in the furnace cover plate. While such a flame is maintained above the furnace, gradually increase the temperature by a suitable adjustment of gas and air to 800° C., then reduce the rate of heat increase to not less than 5° C. and not more than 10° C. per minute. Maintain this rate until the end of the test. It is also important that the 6 in. reducing flame be maintained at the furnace vent throughout the test, if possible, and at all events up to a temperature of 1450° C. Temperatures above 1450° C. require larger proportions of air to gas; however, a strongly reducing atmosphere is not so essential at the higher temperatures, as refractory ashes, owing to their low iron-oxide content, are only slightly affected by oxidizing or reducing atmospheres. After a test has been completed, turn the supply of gas and air off gradually to avoid cracking the muffle crucible.

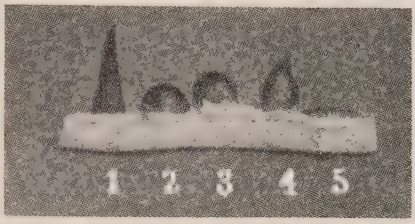


FIG. 236.—Typical Forms of Cones Fused in the No. 3 Melter's Furnace.

The softening temperature is defined as the temperature at which the cone has fused down to a spherical lump, as shown in cones 2 and 3 of Fig. 236. Cone 4 has almost reached the softening temperature.

NOTES.—Critical points other than the softening temperature, that may be observed during the test, and which may be of value are as follows:

The Initial Deformation Temperature.—The temperature at which the first rounding or bending of the apex of the cone takes place, as shown in cone 1 of Fig. 236. Such bending must not be confused with a shrinking or warping of the cone.

The Fluid Temperature.—The temperature at which the cone has spread out over the base in a flat layer, as represented by cone 5 of Fig. 236.

ULTIMATE ANALYSIS

(*For Coal and Coke*)

CARBON AND HYDROGEN

Method With Gas-Heated Combustion Furnace

The determination of carbon and of hydrogen shall be made with a weighed quantity of the sample in a 25-burner combustion furnace of the Glaser type. The products of combustion shall be thoroughly oxidized by passing them over red-hot CuO and $PbCrO_4$, and shall be fixed by absorbing the water in a weighed Marchand tube filled with granular $CaCl_2$ and by absorbing the CO_2 in a Liebig bulb containing a 30% solution of KOH.

Apparatus.—The apparatus used shall consist of a purifying train in duplicate, a combustion tube in the furnace, and an absorption train.

(*a*) The purifying train shall consist of the following purifying reagents arranged in order of passage of air and oxygen through them: H_2SO_4, KOH solution, soda lime, and granular $CaCl_2$. One of the trains is for air and one for oxygen. In the H_2SO_4 and KOH scrubbing bottles the air and the oxygen

shall be made to bubble through about 5 mm. of the purifying reagent. Both purifying trains shall be connected to the combustion tube by a Y-tube, the joint being made tight by a rubber stopper.

(*b*) The combustion tube shall be made of hard Jena glass, or its equivalent. Its external diameter shall be about 21 mm., and its total length 1 meter. The first 30 cm. of the tube shall be empty; following this empty space is an asbestos plug (acid-washed and ignited) or in its place a roll of oxidized copper gauze may be used; the next 40 cm. shall be filled with " wire " CuO; a second asbestos plug separates the copper oxide from 10 cm. of fused $PbCrO_4$, which shall be held in place by another asbestos plug 20 cm. from the end of the tube. The end of the tube shall be drawn out for rubber-tubing connection with the absorption train.

(*c*) The absorption train shall consist of a Marchand tube filled with granular $CaCl_2$ to absorb moisture. The $CaCl_2$ should be saturated with CO_2 before uxing. The Marchand tube shall be followed by a Liebig bulb containing a 30% KOH solution, in which any possible impurities, as ferrous iron or nitrates, have been oxidized by a little $KMnO_4$. A guard tube, containing granular $CaCl_2$ and soda lime, shall be attached to the Liebig bulb to absorb any CO_2 escaping the KOH solution and any water evaporating from that solution.

Procedure.—Connect the train to an aspirator which draws the products of combustion through the entire train. A guard tube of $CaCl_2$ prevents moisture from running back into the absorption train. Maintain the suction constant by a Mariotte flask. The advantage of aspirating the gases through the train rather than forcing them through by pressure is that the pressure on the rubber connections is from the outside, so that gas-tight connections are more easily maintained than if the pressure is on the inside of the tube. Make the connections as tight as possible. The usual test for tightness is to start aspiration at the rate of about three bubbles of air per second through the potash bulb, and then to close the inlet for air and oxygen at the opposite end of the train; if there is no more than one bubble per minute in the potash bulb, the apparatus shall be considered tight.

Before starting a determination when the train has been idle some hours, or after any changes in chemicals or connections, run a blank by aspirating about 1 liter of air through the train, which is heated in the same manner as if a determination on the sample were being made. If the Liebig bulb and the tube containing calcium chloride show a change in weight of less than 0.5 mg. each, the apparatus is in proper condition for use.

Use a porcelain or platinum boat provided with a glass weighing tube of suitable size, which is fitted with an accurately ground glass stopper. Weigh the tube and empty boat. Quickly place in the boat approximately 0.2 g. of the air-dry sample (passing a 250-micron (No. 60) sieve and finer, or better, passing a 149-micron (No. 100) sieve if much free impurity is present). Place the boat at once in the weighing tube, which is quickly stoppered to prevent moisture change in the sample while weighing, and transfer to the furnace. Connect the absorption tubes and transfer the boat and sample from the weighing tube to the combustion tube, which should be cool for the first 30 cm. The CuO should be red hot and the $PbCrO_4$ at a dull-red heat. Transfer the boat from the weighing tube to the combustion tube as rapidly as possible.

As soon as the boat is in place near the asbestos plug at the beginning of the copper oxide insert the stopper connecting with the purifying train and start the aspiration with pure oxygen gas at the rate of three bubbles per second. Turn on one burner about 10 cm. back from the boat, and continue the aspiration carefully until practically all the moisture is expelled from the sample. Then increase the heat very gradually until all the volatile matter has been driven off. In driving off the volatile matter the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar, which may either escape complete combustion or may be driven back into the purifying train. Increase the heat slowly by turning on more burners under the open part of the tube until the sample is ignited; then the temperature may be increased rapidly, but care should be taken not to melt the combustion tube.

Any moisture collecting in the end of the combustion tube or in the rubber connection joining it to the $CaCl_2$ tube may be driven over into the $CaCl_2$ tube by carefully warming with a piece of hot tile. Continue the aspiration with oxygen for 2 minutes after the sample ceases to glow, then turn off the heat and aspirate about 1200 ml. of air. Disconnect the absorption bulbs, wipe with a clean cloth, and allow to cool to the balance-room temperature before weighing.

Calculate the percentages of hydrogen and carbon as follows:

$$\text{Percentage of hydrogen} = 11.19 \times \frac{(\text{increase in weight of } CaCl_2 \text{ tube})}{\text{Weight of sample}}$$

$$\text{Percentage of carbon} = 27.27 \times \frac{(\text{increase in weight of KOH bulb})}{\text{Weight of sampl}}$$

Weigh the ash in the boat and carefully inspect it for any unburned carbon, which would destroy the value of the determination.

Method with Electrically-Heated Combustion Furnace

(*a*) **Apparatus.**—An electrically-heated combustion furnace of the Heraeus type is used by the Bureau of Mines.[26] It consists of three independent heaters, two of which are provided with sheave wheels, and are mounted on a track so that they are movable along the tube; the third heater which surrounds the $PbCrO_4$, is stationary.

(*b*) The furnace as provided by the manufacturer does not include the small stationary heater. This may be made in the laboratory by winding an alundum tube 12 cm. in length with No. 20 nichrome II wire and enclosing it in a cylinder packed with magnesia-asbestos. The movable heaters have very thin platinum foil. weighing about 9 g. in all, wound on a porcelain tube of 30 mm. internal diameter. The larger one which heats the CuO, is 350 mm. in length, and the smaller one, which heats the sample in the boat, is 200 mm. in length.

(*c*) The Jena glass or fused silica combustion tube, of about 21 mm. external diameter and 900 mm. in length, is supported by an asbestos-lined nickel trough. The current through each heater shall be regulated independently by separate rheostats, mounted on the frame of the furnace. The two platinum-wound heaters require an average current of about 4.5 amperes at a pressure of 220 volts, although for heating rapidly a larger amperage is necessary.

[26] U. S. Bureau of Mines Technical Paper No. 8, p. 20 (1929).

Procedure.—Purify the oxygen or air entering the combustion tube by passing through a Tauber's drying apparatus, which contains the following reagents arranged in order of the passage of air or oxygen through them: H_2SO_4, for removing possible traces of ammonia, 30% KOH solution, granular soda lime, and granular $CaCl_2$. Connect one side of the train directly to a Linde oxygen tank provided with a reducing valve for regulating the oxygen pressure; use the other side of the train for purifying the air supply.

The absorption train shall consist of a 5 in. U-tube, filled with granular $CaCl_2$ to absorb moisture. Before using, saturate the $CaCl_2$ with CO_2 to avoid possible absorption of CO_2 during a determination by any traces of CaO that may be present. This saturating is done most conveniently by placing a quantity of $CaCl_2$ in a large drying jar, and filling the jar with CO_2. After standing over night, draw dry air through the jar to remove the CO_2. Keep the treated $CaCl_2$ in well-stoppered bottles.

Connect the $CaCl_2$ tube to a Vanier potash bulb containing a 30% KOH solution and granular $CaCl_2$. Six to eight determinations may be made without recharging this bulb. Connect the potash bulb to an aspirator through a guard tube containing granular $CaCl_2$ and soda lime, and a Mariotte flask. The Mariotte flask keeps the pressure constant.

In general, the method of determination is the same as the one used with the gas furnace as previously described. By moving the heaters toward the end of the tube where the gases enter, and cutting in the electric current, the air may be warmed enough to thoroughly dry the tube and its contents. Cut off the current from the small heater, and move the large heater over the CuO; keep exposed about 250 mm. of that part of the combustion tube between the two heaters where the boat containing the sample is to be placed. Turn the full current on the large heater to bring the CuO to a red heat. When this temperature is reached it is necessary to reduce the current with the rheostat to avoid melting the tube. In the meantime, weigh and connect the absorption train and place the boat containing the sample in the exposed and cooler part of the tube between the two heaters.

Pass the current through the shorter heater. By manipulating the rheostat and by gradually pushing this heater toward the boat, the rate of evaporation of moisture and evolution of volatile matter may be readily controlled.

After combustion is complete, turn the electric current off the smaller heater and move this heater back, to allow the tube to cool for the next determination. Conduct the final aspiration of air and the weighing of the absorption train as described in the Sections under the gas-furnace method.

Note.—In place of granulated $CaCl_2$, concentrated H_2SO_4 may be used for collecting the water formed by combustion. In such cases the air and oxygen entering the combustion tube and the gas leaving the potash bulb must also be dried by H_2SO_4.

Other suitable forms of absorption vessels than those indicated in the above procedure may be used.

NITROGEN

The Kjeldahl-Gunning method is recommended for the determination of nitrogen. This method has the advantage over either the simple Kjeldahl or the Gunning method, in requiring less time for the complete oxidation of the organic matter, and in giving the most uniform results.

The Kjeldahl-Gunning Method.—Boil 1 g. of the sample with 30 ml. of concentrated H_2SO_4, 7 to 10 g. of K_2SO_4, and 0.6 to 0.8 g. of metallic mercury in a 500-ml. Kjeldahl flask until all particles of the sample are oxidized and the solution nearly colorless. Continue the boiling at least 2 hours after the solution has reached the straw-colored stage. The total time of digestion will be from 3 to 4 hours except in the case of coke and anthracite coal which require much longer digestion. The addition of a few crystals of $KMnO_4$, after the solution has cooled enough to avoid violent reaction, tends to insure complete oxidation. Coke and anthracite coal should be ground to an impalpable powder, as they are very difficult to oxidize. Even if this is done the digestion may require 12 to 16 hours.

After cooling, dilute the solution to about 200 ml. with cold water. If the dilution with water has warmed the solution, cool it again and add the following reagents: 25 ml. K_2S solution (40 g. K_2S per liter) to precipitate the mercury, 1 to 2 g. of granular zinc to prevent bumping, and finally enough strong NaOH solution (usually 80 to 100 ml.) to make the solution distinctly alkaline. The danger of loss of NH_3 may be minimized by holding the flask in an inclined position while the NaOH solution is being added. The alkaline solution runs down the side of the flask and forms a layer below the lighter acid solution. After adding the alkaline solution, connect the flask at once to the condensing apparatus and mix the solution by gently shaking the flask.

Distill the NH_3 over into a measured amount (10 ml.) of standard H_2SO_4 solution, to which has been added sufficient cochineal indicator for titration. Care should be taken that the glass connecting tube on the end of the condenser dips under the surface of the standard acid. Distill the solution slowly until 150 to 200 ml. of distillate has passed over. To avoid mechanically entrained alkali passing over into the condenser, the rate of distillation should not exceed 100 ml. per hour. Titrate the distillate with standard NH_3 solution (20 ml. NH_4OH solution = 10 ml. H_2SO_4 solution = 0.05 g. nitrogen). Standard NaOH or KOH solution with methyl orange or methyl red as indicator may be used instead of NH_3 and cochineal.

A blank determination shall be made in exactly the same manner as described above, except that 1 g. of pure sucrose (cane sugar) shall be substituted in place of the sample. The nitrogen found in this blank determination shall be deducted from the result obtained with the sample.

The K_2S and NaOH may be dissolved in a single stock solution. Dissolve sufficient K_2S in the water before adding the NaOH, to make a solution in which the quantity necessary for a nitrogen determination (80 to 100 ml.) contains 1 g. of K_2S. Twelve grams of K_2S and 500 g. of NaOH in one liter of water, are required for the above proportions.

OXYGEN

There being no satisfactory direct method of determining oxygen it shall be computed by subtracting the sum of the percentages of hydrogen, carbon, nitrogen, sulfur, water and ash from 100. The result so obtained is affected by all the errors incurred in the other determinations and especially by the change in weight of the ash-forming constituents on ignition. In the case of

coal, iron pyrite changes to ferric oxide, increasing the ash and causing a negative error in the oxygen equivalent to three-eights of the pyritic sulfur. On the other hand, there is always a loss on ignition, of water of composition from the clayey and shaley constituents, CO_2 from carbonates, etc., which tends to compensate the absorption of oxygen.

Corrected Oxygen (for Coal).—When a more correct oxygen value is desired, it may be obtained by making the corrections indicated in the following formula:

$$\text{Corrected oxygen} = 100 - [(C - C') + (H - H') + N + H_2O + S' + \text{corrected ash}]$$

where C = total carbon;
C' = carbon of carbonates;
H = total hydrogen less hydrogen of water;
H' = hydrogen from water of composition in clay, shale, etc.,
N = nitrogen;
H_2O = moisture as found as 105° C.;
S' = sulfur not present as pyrite or sulfate. This is usually small. In many types of coal it may be disregarded.
Corrected ash = mineral constituents originally present in the coal. For most purposes this can be determined with sufficient accuracy by adding to the ash, as found, five-eighths of the weight of pyritic sulfur, the CO_2 of carbonates and the water of composition of clay, shale, etc. See also Determination of Ash, Sections 10 and 11.

Calorimetric Determination

(For Coal and Coke)

Apparatus: (*a*) ***Combustion Bombs.***—The Atwater, Davis, Emerson, Mahler, Parr, Peters, Williams, or similar bombs may be used. The bomb shall have an inner surface and accessory fittings, including crucible, of platinum, gold, porcelain enamel, or other material which is not attacked by HNO_3 and H_2SO_4, or other products of combustion.

(*b*) ***Calorimeter Jacket.***—The calorimeter shall be provided with a water-jacket having a cover to protect the calorimeter from air currents. The jacket shall be kept filled with water within 2 or 3° C. of the temperature of the room (except in calorimeters which are totally submerged, where the jacket temperature is controlled by a thermostat) and should be stirred continuously by some mechanical stirring device.

(*c*) ***Stirring of the Calorimeter Water.***—The water in the calorimeter shall be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. A motor-driven screw or turbine stirrer is recommended and the speed should not be excessive. This may be determined by adjusting the temperature of the calorimeter to equality with that of the jacket and allowing the stirrer to run continuously for 10 minutes. If the temperature of the calorimeter rises more than about 0.01° C. in this length of time, the rate of stirring is excessive. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is irregular. The portion of the

stirring device immersed in the calorimeter should be separated from that outside by non-conducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

(*d*) ***Thermometers.***—Thermometers used shall have been certified by a government testing bureau and shall be used with the corrections given on the certificate. This shall also apply to electrical resistance or thermo-electric thermometers. Correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the "setting" of Beckmann thermometers. For accurate work, either Beckmann or special calorimetric thermometers graduated to 0.01° or 0.02° C. are required. Such thermometers should be tapped lightly just before each reading to avoid errors caused by the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

(*e*) ***Oxygen.***—The oxygen used for combustions shall be free from combustible material. The total amount of oxygen contained in the bomb for combustion shall not be less than 5 g. per gram of the sample. But the combustion must be complete, as shown by the absence of any sooty deposit on opening the bomb after firing.

(*f*) ***Firing Wire.***—The sample in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used, it should be of about No. 34 B. & S. gage and not more than 10 cm. (preferably 5 cm.) should be used at a time. A correction of 1600 calories per gram weight of iron wire burned shall be subtracted from the observed number of calories.

(*g*) ***Standardization.***—The water equivalent of a calorimeter can best be determined by the use of the standard combustion samples supplied by the U. S. Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of standard samples supplied by the Bureau of Standards, and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of either the same or different standard materials. The conditions as to the amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made shall be the same as for combustions of the sample. In the case of any disagreement between contracting parties a check standardization may consist of two or more combustions of standardizing samples.

Procedure: (*a*) ***Preparation of Sample.***—The ground sample shall be thoroughly mixed in the bottle and an amount, approximately 1 g., shall be taken out and weighed in the crucible in which it is to be burned. Samples which are likely to be blown out of the crucible should be briqueted. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation in the use of naphthalene for standardization.

(*b*) ***Preparation of the Bomb.***—The firing wire, if iron, shall be measured and coiled in a small spiral and connected between the platinum terminals,

using, if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron shall both be clean. About 0.5 ml. of water should be placed in the bottom of the bomb to saturate with moisture the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the sample or briquet of standard material. For the combustion of standardizing samples iron wire is preferable to platinum.

(*c*) ***Filling the Bomb with Oxygen.***—Oxygen from the supply tank shall be admitted slowly to avoid blowing the sample from the crucible without displacing the original air content, and the pressure allowed to reach 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs, so that the bomb shall contain an amount of oxygen sufficient for complete combustion, namely, at least 5 g. per gram of the sample. This method of filling should insure sufficient nitrogen for complete oxidation of the sulfur in the coal.[27]

(*d*) ***Calorimeter Water.***—The calorimeter shall be filled with the required amount of distilled water, depending upon the type of calorimeter. The amount may be determined either by measurement in standardized flask or by weighing. The amount shall be kept the same as that used in the standardization of the apparatus.

(*e*) ***Temperature Adjustments.***—The initial temperature in the calorimeter shall be so adjusted that the final temperature, after the combustion, will not be more than 1° C., preferably about 0.5° C., above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be small when the rise of temperature is 2° or 3° C., and the effect of evaporation will also be small.

(*f*) ***Firing Current.***—The electric current used for firing the charge shall be obtained from storage or dry cells having an electromotive force of not more than 12 volts. A higher voltage is liable to cause an arc between the firing terminals, introducing additional heat, which cannot be measured with certainty. The circuit should be closed by means of a switch which should remain closed for not more than 2 seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out.

(*g*) ***Method of Making an Observation.***—The bomb when ready for firing, shall be placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer shall then be started and after the thermometer reading has become steady, not less than 2 minutes after the stirrer is started, temperatures shall be read at 1-minute intervals for 5 minutes and the charge then fired, the exact time of firing being noted. Observations of temperature shall then be made at intervals depending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings shall be taken at 1-minute intervals for 5 minutes to determine the final cooling rate.

(*h*) ***Titration.***—After a combustion and after allowing the gas to escape the bomb shall be opened and the inside examined for traces of unburned material

[27] S. H. Regester, "Oxidation of Sulfur Compounds of Coal, and of Nitrogen in the Bomb Calorimeter, and the Correction to be Applied in Determining the Heating Value of Coal," Industrial and Engineering Chemistry, **6**, 812 (1914).

or sooty deposit. If these are found, the observations shall be discarded. If the combustion appears complete, the bomb shall be rinsed out thoroughly and the washings titrated with a standard alkali solution (1 ml. = 0.02173 g. HNO_3 = 5 calories) using methyl-orange or methyl-red indicator, to determine the amount of acid formed. A correction of 230 calories per gram of HNO_3 should be subtracted from the total heat observed. An additional correction of 1300 calories per gram of sulfur in the sample should be made for the excess of difference in heats of formation of SO_2 and aqueous H_2SO_4 over the heat of formation of aqueous HNO_3.

Calculation of Results: The following method of calculation is recommended to take the place of the Pfaundler or other similar formulas for calculating the cooling correction (radiation correction):

Observe (1) the rate of rise, r_1, of the calorimeter temperature in degrees per minute for 5 minutes before firing; (2) the time, a, at which the last temperature reading is made immediately before firing; (3) the time, b, when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing, 60% of the expected [28] temperature rise, and noting the time at which this point is reached); (4) the time, c, of a thermometer reading taken when the temperature change has become uniform some 5 minutes after firing; (5) the final rate of cooling, r_2, in degrees per minute for 5 minutes.

Multiply the rate r_1 by the time $b-a$ in minutes and tenths of a minute, and add to this product (subtracted if the temperature was falling at the time a) to the thermometer reading taken at the time a. Multiply the rate r_2, by the time $c-b$ and add this product (subtracted if the temperature was rising at the time c and later) to the thermometer reading taken at the time c. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated. Divide this result, corrected for the heats of formation of HNO_3 and H_2SO_4 observed and for the heat of combustion of the firing wire, when that is included, by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the British thermal units per pound. (See example.)

Note.—In practice, the time $b-a$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

The results shall be reduced to calories per gram or British thermal units per pound of *dry sample*, the moisture being determined upon a sample taken from the bottle at about the same time as the combustion sample is taken.

[28] When the temperature rise is not approximately known beforehand, it is only necessary to take thermometer readings at 40, 50, 60 seconds (and possibly 70 seconds with some calorimeters) after firing, and from these observations to find when the temperature rise had reached 60% of the total. Thus, if the temperature at firing was 2.135° C., at 40 seconds 3.05°, at 50 seconds 3.92°, at 60 seconds 4.16°, and the final temperature was 4.200°, the total rise was 2.07°; 60% of it was 1.24°. The temperature to be observed was then 2.14°+1.24°=3.38°. Referring to the observations at 40 and 50 seconds, the temperatures were respectively 3.05 and 3.92°. The time corresponding to the temperature of 3.38° was, therefore:

$$40+\frac{3.38-3.05}{3.92-3.05}\times 10=44 \text{ seconds.}$$

Example.—

OBSERVATIONS.

Water equivalent = 2550 g.
Weight of charge = 1.0535 g.
Approximate rise of temperature expected = 3.2° C.
60% of approximate rise = 1.9° C.

Time	Thermometer Readings, Deg. Cent.	Corrected Temperature (or corrected Beckmann thermometer readings)
10–21	15.244	Thermometer corrections taken from the certificate
22	15.250	
23	15.255	
24	15.261	
25	15.266	
(*a*) 26	15.272	15.276° C.
		Charge fired
(*b*) 27.2	17.2[a]	
(*c*) 31	18.500	18.497° C.
32	18.498	
33	18.497	
34	18.496	
35	18.494	
36	18.493	

[a] The initial temperature is 15.27° C.; 60% of the expected rise is 1.9° C. The reading to observe is then 17.2° C.

CALCULATION

$r_1 = 0.028° \div 5 = 0.0056°$ per minute. $b - a = 1.2$ minutes.		
The corrected initial temperature is $15.276° + 0.0056° \times 1.2$	$= 15.283°$	
$r_2 = 0.007° \div 5 = 0.0014°$ per minute; $c - b = 3.8$ minutes		
The corrected final temperature is $18.497° + 0.0014° \times 3.8$	$= 18.502°$	
Total rise $18.502° - 15.283°$	$= 3.219°$	
Total calories 2550×3.219	=	8209
Titration, etc.		−7
Calories from 1.0535 g. sample		8202
Calories per gram	7785	
or British thermal units per pound	14013	

The result obtained by the above method of computation and determination is the total heat of combustion at constant volume, with the water in the products of combustion condensed to liquid at the temperature of the calorimeter, that is, about 20 to 35° C.

Net heat of combustion at 20°, shall refer to results corrected for latent heat of vaporization, as follows:

Total heat of combustion in B.t.u. − 1040 (total hydrogen × 9) = net heat of combustion in B.t.u. per pound.

Also:

Total heat of combustion in calories − 580 (total hydrogen × 9) = net heat of combustion in calories per gram.

NOTES.—For anthracite, coke, and coal of high ash content, which do not readily burn completely, the following procedure is recommended:

The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles. The sample is then sprinkled evenly over the surface of the asbestos. Otherwise the procedure is as previously described.

The method of computing the "cooling correction" described in U. S. Bureau of Mines Technical Paper No. 8, pp. 26–30 (1929), may also be used.

Tolerances: The permissible differences between two or more determinations shall not exceed the values as specified.

	Permissible Same Laboratory	Differences Different Laboratories
A. On Laboratory Samples, Crushed to Pass Through an 840-Micron (No. 20) Sieve.		
Moisture:		
Under 5%	0.2	0.3
Over 5%	0.3	0.5
B. On Laboratory Samples, Crushed to Pass Through a 250-Micron (No. 60) Sieve.		
1. Moisture:		
Under 5%	0.2	0.3
Over 5%	0.3	0.5
2. Ash:		
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12% of ash, containing carbonate and pyrite	0.5	1.0
3. Volatile Matter:		
Bituminous coals	0.5	1.0
Lignites	1.0	2.0
Cokes	0.2	0.4
4. Sulfur:		
Coal, Under 2%	0.05	0.10
Coal, Over 2%	0.10	0.20
Coke	0.03	0.05
5. Ultimate Analysis:		
Carbon	0.3	...
Hydrogen	0.07	...
Nitrogen	0.05	...
6. Calorimetric Determination:		
Permissible differences in per cent	0.3	0.5
7. Fusibility of Coal Ash:		
Permissible differences in deg. Cent	30	50

ANALYSIS OF EXPLOSIVES [1]

The methods described in this chapter cover all of the more common types of explosives employed in the United States for both commercial and military purposes. Those of chief commercial importance are black powder, nitroglycerin dynamites, including "straight" dynamites, ammonia dynamites, gelatin dynamites, and low-freezing dynamites, "Permissible" coal mining explosives and nitrostarch blasting explosives. Military explosives include smokeless powder, guncotton, trinitrotoluene, picric acid, ammonium picrate, "Amatol," tetryl and tetranitroaniline. No sharp distinction can, however, be drawn between commercial and military explosives, as many are utilized for both purposes. Many tons of surplus TNT on hand at the end of the World War were used in commercial work; nitrostarch explosives found important application for military use during the war; mercury fulminate, lead azide, and other detonators and priming compositions are essential in every field of explosives.

The methods described have largely been used by the writer in practical explosives testing and analysis in connection with both Government and private work. Most of those applying to commercial explosives have been approved by the United States Bureau of Mines for use in its Explosives Chemical Laboratory.[2]

BLACK POWDER

The composition of black powder varies to some extent, depending chiefly on the purpose for which the explosive is to be used. Black blasting powder contains sodium nitrate, charcoal and sulfur; black gunpowder is quite similar except that potassium nitrate is generally substituted for the sodium nitrate; black fuse powder is similar to the latter, differing mainly in its granulation. The same general method of analysis is therefore applicable to all types of black powder.

Sampling.—From 50 to 100 grams of the original sample is crushed in small portions in a porcelain mortar and completely passed through an 80-mesh

[1] Chapter by C. G. Storm. Published by permission of Chief of Ordnance, U. S. A.

[2] See Bureau of Mines Bulletin No. 51, "The Analysis of Black Powder and Dynamite," W. O. Snelling and C. G. Storm, 1913, Bulletin No. 96, "The Analysis of Permissible Explosives," C. G. Storm, 1916, Bulletin No. 219, "Explosives, their Materials, Constitution and Analysis," C. A. Taylor and W. H. Rinkenbach, 1923, and Tech. Paper No. 282, "Analysis of Detonating and Priming Mixtures," C. A. Taylor and W. H. Rinkenbach, 1922.

sieve, care being taken to avoid undue exposure to the air. The separate powdered portions are promptly bottled and the entire sample is finally well mixed.

Moisture.—The standard method of the Bureau of Mines is to desiccate a 2-gram sample on a 3-inch watch glass over sulfuric acid for three days, the loss of weight being moisture. It has been shown, however, that equally accurate results can be obtained by drying at 70° C. in a constant temperature oven to constant weight, for which 2–3 hours is usually sufficient. As much as 5 hours drying at 70° C. will not cause loss of sulfur. Drying at 100° C. gives results which are slightly high, due to loss of sulfur.

Nitrates.—About 10 grams of the finely ground sample in a Gooch crucible provided with an asbestos mat, is extracted with warm water by means of suction, the water being added in 15–20 ml. portions and each portion being allowed to stand in the crucible a short time before suction is applied. About 200 ml. of water is usually sufficient, but the last drops of filtrate should be tested by evaporation to ensure the absence of nitrates. A blue color on the addition of sulfuric acid containing a few crystals of diphenylamine will also indicate the presence of nitrates.

The water extract includes a small amount of water-soluble organic material from the charcoal in addition to the nitrate. It is made up to 250 ml. and an aliquot portion (50 ml.), evaporated to dryness on the steam bath, treated with a little nitric acid, again evaporated, heated to slight fusion and weighed.

If allowance for impurities in the nitrate is desired, a direct determination of nitrate may be made on a separate portion of the water extract by the Devarda method or by means of the nitrometer, but for all practical purposes the evaporation method is sufficient. The usual tests should be made to determine whether sodium nitrate or potassium nitrate is present.

Some black powders contain barium nitrate in addition to potassium nitrate. Barium nitrate, if present, is determined in an aliquot portion of the water extract by precipitating with sulfuric acid and weighing the precipitate of barium sulfate.

The residue left in the crucible, consisting of sulfur and charcoal, is dried at about 70° C. to constant weight (for 5 hours or over night if more convenient), the loss of weight minus the moisture content being the water-soluble portion. This result serves as a check on the evaporation result.

Sulfur.—The residue in the crucible is extracted in a Wiley extractor or other continuous extraction apparatus with carbon disulfide, until evaporation of a small portion of the solvent passing through the crucible shows absence of sulfur. The excess of carbon disulfide is then allowed to evaporate from the crucible in a warm place away from flame, and the residue finally dried to constant weight at 100° C. The loss of weight is considered as sulfur.

Charcoal.—The dry residue in the crucible should consist only of charcoal.

Ash.—The ash in the charcoal may be determined by ignition over a Bunsen burner until all of the carbon has been burned off, and weighing. This ash also contains, of course, any non-volatile matter that may have been present in the sulfur and nitrate. An ash content in excess of 1% (calculated on the weight of powder taken for analysis) may be regarded as an indication of incomplete extraction of nitrate.

Calculation of Results.—Since a portion of the charcoal is always dissolved in the water extract, it is customary to express the content of charcoal by subtracting the sum of the following from 100%:

% Moisture (by desiccation or drying at 70° C.).
% Nitrate (by evaporation of water extract with HNO_3).
% Sulfur (by loss on extraction with CS_2).

NITROGLYCERIN DYNAMITES

" Straight " Dynamite

So-called " Straight " nitroglycerin dynamite has been manufactured to only a relatively small extent in this country for a number of years. This was due in part to wartime developments in the manufacture of both ammonium nitrate and nitrocompounds, and in part to the high price of glycerin, which reached its maximum about the early part of 1927. During recent years the use of ethylene glycol dinitrate (more commonly called nitroglycol) as a substitute for a considerable part of the nitroglycerin in various types of dynamites and " permissible explosives " has greatly decreased the amount of straight dynamites manufactured. " Straight " nitroglycerin dynamites are still used to some extent, however, particularly where quick-acting dynamites of high strength are required, as in blasting in hard rock. They consist essentially of nitroglycerin absorbed in a " dope " composed of a combustible absorbent, usually wood pulp, and an oxidizing material (sodium nitrate), to which has been added a small amount of an antacid (calcium carbonate, zinc oxide, etc.). The analysis is best carried out by successive extractions, usually with ether, water and hydrochloric acid.

Sampling.—The wrappers are removed from a number of the cartridges, and from 3 to 5 cm. of the ends of the exposed roll of explosives rejected. The remainder is thoroughly mixed on a large sheet of paraffined paper or in a large porcelain dish, and an average sample selected and bottled—usually about one half pound. The importance of thorough mixing of the sample must not be overlooked, in view of the fact that there is frequently a decided tendency for the nitroglycerin to segregate due to insufficient or unsuitable absorbent, so that this liquid ingredient may not be uniformly distributed throughout the cartridge. Also if a carefully mixed sample has been allowed to stand for some days, especially in a warm place, segregation may occur in the bottle, so that it is advisable to mix the sample again before analysis.

Qualitative Examination.—Although a qualitative analysis of a sample known to be straight nitroglycerin dynamite is usually unnecessary, the exact nature of the sample may be unknown, and a knowledge of the composition of some of the more complex types of dynamite is necessary before a quantitative analysis can be properly conducted.

About 25 grams of the sample is shaken with several successive portions of ether in a large stoppered test tube, the ether being decanted off through a filter paper and the residue finally washed on the filter. The ether solution is allowed to evaporate slowly on a steam bath and the filter paper spread out on a glass plate in an oven so that the residue may dry quickly. The evaporated ether extract may contain nitroglycerin, sulfur (especially in the lower grades of dynamite), rosin, vaseline, or paraffin oil (in ammonia dynamite), nitrotoluenes and other nitrocompounds (in low-freezing dynamites), etc.

Nitroglycerin is readily detected by shaking a drop of the liquid with one or two ml. of concentrated H_2SO_4 and about 1 ml. of mercury in a test tube, an evolution of brown fumes of nitric oxides being noted if nitroglycerin is present. A similar reaction is, however, given by nitroglycol, so that this test will not distinguish between straight nitroglycerin and a mixture of nitroglycerin and nitroglycol. The latter substance (ethylene glycol dinitrate) has, when pure, almost the same nitrogen content as nitroglycerin (18.42% as compared with 18.50%). Its presence is indicated by a continual loss in weight of the ether extract in attempting to dry it to constant weight. This loss is more rapid in a vacuum. Sulfur will appear as crystals in the evaporated extract, and may be identified by removing them, washing with acetic acid, and noting the odor of SO_2 on heating in a flame. Rosin, vaseline, oils, etc., appear as a greasy scum on the surface of the nitroglycerin or adhering to the walls of the beaker. These substances, like sulfur, are practically insoluble in acetic acid (70%), and may be separated from the nitroglycerin by means of this solvent. Trinitrotoluene will appear in the nitroglycerin as long yellowish needles, which may be removed, recrystallized from alcohol, and identified by their melting point (approx. 80° C.), or by the red color produced when the alcoholic solution is treated with a little caustic soda solution.

The residue insoluble in ether is replaced in the test tube and treated with water in a similar manner until all water-soluble material has been dissolved. The water solution is tested for sodium, potassium, barium, zinc, etc., and for nitrates, chlorides, etc., using the general methods of qualitative analysis.

The residue is again treated with cold dilute HCl, any effervescence being noted as indicating the presence of a carbonate, and the resulting solution tested for calcium, magnesium, zinc, etc., which may have been present as carbonates or oxides for the purpose of serving as antacids.

The residue insoluble in ether, water, and cold acid may contain wood pulp, starchy cereal products, sawdust, nitrocellulose, ground vegetable ivory (button waste), kieselguhr, ground nut shells, etc. It is most conveniently examined by means of a low-power microscope, whereby its constituents are usually readily determined. Starch is easily detected by heating a portion to boiling with dilute acid, cooling and adding a few drops of iodine solution (in KI), a blue coloration indicating starch.

Moisture.—Moisture is best determined by desiccation over sulfuric acid, a sample of about 2 grams being spread evenly over the surface of a 3-inch watch glass and desiccated for 3 days. Continued desiccation causes a gradual loss of nitroglycerin, but the 3-day loss may be safely assumed to closely represent the actual moisture content. The time of the determination may be greatly shortened by the use of a vacuum desiccator, in which case 24 hours desiccation will give a close approximation to the true moisture content.

It must be remembered that in determining moisture in the presence of nitroglycerin, some volatilization of the latter is unavoidable, and that therefore the method followed must be an empirical one. An attempt to desiccate the sample to constant weight will show that there is undoubtedly a continual loss of nitroglycerin. This has been demonstrated [3] by a series of weighings of a sample exposed for a period of 459 days at a constant temperature of 33°–35° C. in an empty desiccator containing no desiccating agent. A gradual loss resulted during the entire period, totaling 17.52% of the original weight of the sample, the original moisture content of which was about 1%.

Extraction with Ether.—Ether removes from dynamite not only the nitroglycerin, but, as has already been mentioned, sulfur, resins (present as a component or as a constituent of the wood pulp), oils (usually from cereal products present), etc. Nitrotoluenes, nitroglycol, paraffin, vaseline, etc., are not normal constituents of straight dynamite and are considered under the type of explosive in which they are most likely to occur.

Reflux Condenser Method.—From 6 to 10 grams of the sample is weighed in either a porcelain Gooch crucible with asbestos mat or a porous alundum filtering crucible of about 25 ml. capacity. The asbestos mat is best prepared as follows: A mixture of 1 liter of water and 5 grams of previously ignited and shredded short fibre asbestos free from hard lumps and very fine material is well shaken and about 10 ml. poured into the crucible. Suction is applied and a smooth and perfect mat almost invariably results. The crucibles thus prepared are dried at 100° and are ready for use.

The sample in the extraction crucible is extracted with about 35 ml. of ether (U. S. P.) preferably in a continuous extraction apparatus (Wiley or similar type preferred), for about 45 minutes to 1 hour, water being continuously circulated through the condenser and the extraction tube heated on a water bath, or electric heater, the temperature of which is so regulated that the sample in the crucible will be kept covered with ether without overflowing.

Suction Method.—If desired, the ether extraction may be carried out by suction, the Gooch crucible being held in a carbon tube passing through the stopper in a suction flask. About 100 ml. of ether in 6 to 8 portions is passed through the crucible, each portion being allowed to stand in the crucible for one minute before applying gentle suction. No more air than is necessary should be drawn through the sample in order to avoid condensation of moisture in the sample, which might dissolve a portion of the water-soluble salts. This method uses considerably more ether than the reflux condenser method and its chief advantage is that the apparatus required is more simple.

On completion of the extraction the crucible is at once placed in a drying oven, or the excess ether may be removed by suction before drying. If ammonium nitrate is present the drying should be conducted at 70° C. for 18 hours or overnight, but otherwise 5 hours at 100° C. is ample. The loss of weight represents all ether-soluble material plus the moisture in the original sample.

Evaporation of Ether Extract.—The ether extract is washed out of the extraction tube or suction flask with a little ether into a tared evaporating dish or small beaker and the ether allowed to evaporate spontaneously in a warm

[3] Storm, C. G., "The Analysis of Permissible Explosives," Bulletin No. 96, Bureau of Mines, pages 21–24, 1916.

place, or evaporated by means of the "bell jar evaporator."[4] The latter consists of a tubulated bell jar with openings at top and side, placed on a ground glass plate, a slow current of dry compressed air from two drying cylinders containing H_2SO_4 and soda lime respectively, entering the top opening through a glass tube, the lower end of which extends to about one half inch from the surface of the ether solution in the beaker, which is placed on the glass plate. The dry air current striking the surface of the solution with just enough force to cause a slight "dimple," causes rapid evaporation of the ether, and deposition of moisture in the beaker along with the evaporated residue is avoided. The low temperature produced by the rapid evaporation minimizes the loss of nitroglycerin by volatilization. From 5 to 6 hours is usually required for complete evaporation, which should be determined by check weighings. If the bell jar method is not used, the residue, after removal of the ether, must be desiccated over H_2SO_4 for at least 24 hours in order to remove moisture deposited during evaporation.

Nitroglycerin.—Nitroglycerin is determined in the dried and weighed ether extract from which all ether has been removed as above described. This determination is best made by means of the du Pont modification of the 5-part Lunge nitrometer (see p. 650, Vol. I). The sample is dissolved in 5–10 ml. of pure sulfuric acid (specific gravity 1.84) and transferred to the generating bulb of the nitrometer, the beaker and cup of the nitrometer being washed with several further additions of acid until a total of 20–25 ml. has been used. If the quantity of nitroglycerin present is too great, the sample, dissolved in sulfuric acid, is transferred to a burette and an aliquot part run into the nitrometer. The maximum amount of pure nitroglycerin used for the determination should not exceed 0.75 gram. The determination is carried out in the usual manner and the reading of the gas volume in the graduated reading tube divided by .1850 to find the weight of nitroglycerin in the sample used for the determination (pure nitroglycerin contains 18.50% N).

Sulfur, Resins, Oils, etc.—It is always preferable to carry out the extraction with ether on duplicate samples, using one sample of the extract for the determination of nitroglycerin as above, and the other for determining sulfur, resins, oils, etc., that may also be contained in the ether extract.

The weighed extract is redissolved in a mixture of ether and alcohol, previously neutralized with standard alkali. The solution thus obtained is titrated with standard alcoholic potash solution using phenolphthalein indicator. 1 ml. of tenth normal alkali is equal to 0.034 grams of rosin (colophony).

A large excess of the alcoholic potash is now added and the mixture heated several hours or overnight on the steam bath to saponify the nitroglycerin. Shake with water and ether in a separatory funnel. The ether solution contains paraffin, vaseline, or mineral oils that may be present, and is evaporated and the residue weighed. The water solution is acidified with HCl, and Br added to oxidize any sulfur. Any separated rosin is filtered off and weighed as a check on the titration, and sulfur determined in the filtrate by precipitation as $BaSO_4$.

Sulfur may also be separated from nitroglycerin by means of acetic acid of approximately 70% strength, the nitroglycerin being quite soluble in acetic

[4] Storm, C. G., "The Analysis of Permissible Explosives," Bulletin 96, Bureau of Mines, page 35, 1916.

acid and the sulfur almost insoluble. The sulfur is filtered from the solution, washed slightly with alcohol to remove the acetic acid solution, dried and weighed.

If a considerable quantity of crystals of sulfur is found in the evaporated ether extract, it is possible that all of the sulfur has not been removed by the ether, and in this case an extraction is made with carbon disulfide, in exactly the same manner as the ether extraction. This extraction is made subsequent to the extraction with water, the sulfur being determined by loss of weight of the residue or by direct weight after evaporation of the carbon disulfide away from free flame.

Extraction with Water and Determination of Nitrates.—The dried and weighed residue left in the crucible after extraction with ether, is extracted with water, using a suction flask fitted with a carbon filter tube in which the crucible is held by a short length of thin-walled rubber tubing. Cold water is used for this extraction, as hot water would gelatinize any starch present. A total of at least 200 ml. of water is passed through the sample, in at least 10 portions, each portion being allowed to stand in contact with the residue for a few minutes before being sucked into the flask. An evaporation test of a few drops of the filtrate will determine the completeness of the extraction. When the extraction is complete, the crucible with its insoluble residue is dried for 5 hours, or overnight, at 95°–100° C., and the loss of weight noted as total water-soluble material. This includes nitrates and other soluble salts that may be present, together with water extract from the wood pulp, flour or other absorbent. This soluble organic material may amount to as much as 2% of the total sample, when cereal products are present. Calcium, magnesium, or zinc may also be present in solution, resulting from the action of acid decomposition products of the nitroglycerin on the carbonate or other antacid present. In routine analyses of ordinary dynamite, the loss of weight on extraction with water is usually considered as the alkaline nitrate (sodium or potassium), but where more exact results are desired an aliquot portion of the extract is evaporated to dryness with a little nitric acid to oxidize organic materials, and the residue weighed as alkaline nitrate. This weight may be corrected for inorganic impurities—chlorides, sulfates, iron, aluminum, calcium, etc.—determined separately by the usual methods.

Nitrates may be determined by means of the nitrometer, using an aliquot portion of water extract estimated to contain .6 to .8 gram of $NaNO_3$ or .8 to 1.0 gram of KNO_3. This is evaporated on the steam bath almost to dryness and transferred with as little water as possible, to the cup of the nitrometer. This solution is drawn into the generator and 30 to 40 ml. of 95–96% H_2SO_4 added slowly so as to avoid generating sufficient heat to crack the glass. The generator is then shaken for a total time of 8–10 minutes in order to be certain that the generation of gas is complete with the diluted acid. The gas is measured and the % of nitrate calculated as in the case of nitroglycerin.

Extraction with Acid.—When starch is not present in the residue, a simple extraction of the residue insoluble in water is made with cold dilute HCl (1 : 10), 100 ml. being drawn through the sample in the crucible in small successive portions as described under "Extraction with Water." Several portions of water are then drawn through to wash out the acid, and the residue in the crucible dried for 5 hours at 95° to 100° C. The loss of weight is usually

reported as antacid, but the base dissolved may be determined by the usual quantitative methods if desired. The acid-soluble materials generally present are calcium or magnesium carbonate or zinc oxide.

Determination of Starch.—If starch is present in the residue insoluble in water, it is removed together with the antacid by boiling with dilute acid. The residue is moistened with water, scraped or washed out of the crucible into a 500-ml. beaker, the volume brought to about 250 ml. by the addition of water and 3 ml. of concentrated HCl, and the mixture boiled until a drop of the solution fails to give a blue color when treated on a spot plate with a drop of a solution of iodine in KI. This indicates that the starch has been completely hydrolyzed to dextrin. The mixture is then filtered through a fresh crucible, washed with water, dried and weighed, correction being made for the weight of the asbestos mat of the original crucible.

The antacid dissolved in the acid filtrate is determined as already described. The loss of weight by the boiling treatment, minus the antacid found, represents starch and other dissolved organic materials removed from cereal products or wood pulp. The insoluble residue includes the wood pulp and the crude fibre of the cereal products.

Because of the impracticability of exact separations it is customary to report all of the soluble organic material included in both water and acid extractions as " starch " or " starchy material," and the insoluble organic residue as " wood pulp and crude fibre," or the sum of these organic materials is often reported as " carbonaceous combustible material."

Insoluble Residue and Ash.—The insoluble residue may contain wood pulp or sawdust, the crude fibre from various cereal products such as corn meal, wheat flour, middlings, bran, etc., ground nut shells, vegetable ivory meal, and more rarely inorganic material such as infusorial earth (kieselguhr), clay, etc. These can usually be identified by microscopic examination (see Bureau of Mines Bulletin 96, Page 74), and a determination of the ash will show whether inorganic materials are present. A high ash content may also indicate incomplete water or acid extractions.

Ammonia Dynamite

So-called ammonia dynamite is essentially " straight " dynamite in which a large part of the nitroglycerin is replaced by ammonium nitrate. The ammonium nitrate is frequently protected from moisture by a coating of vaseline or paraffin and is usually neutralized with zinc oxide. This type of dynamite generally contains less wood pulp than the corresponding grades of " straight " dynamite, and sulfur and cereal products, such as low grade flour, are usually present.

The determination of moisture and the various extractions are carried out as described for " straight " dynamite. An extraction with carbon disulfide is usually necessary to effect complete removal of the sulfur; this properly follows the extraction with water. The analysis of the ether extract may be conducted as already described. In drying the residue left in the crucible after extraction with ether, it is important that a temperature of approximately 70° C. be used, because in the presence of ZnO, the loss of ammonium nitrate is considerable at 100° C. Pure ammonium nitrate is not appreciably affected

by even 24 hours heating at 100° C., but the presence of the ZnO causes decomposition at this temperature.

The water extract contains sodium nitrate and ammonium nitrate together with practically all of the zinc oxide present, the latter ingredient being dissolved with the ammonium nitrate, and a small amount of soluble organic material from the flour or other absorbent. It is analyzed as follows: An aliquot portion is evaporated to dryness in a platinum or silica dish on a steam bath, the ammonium nitrate volatilized by careful heating over a burner, a little nitric acid added to re-oxidize any nitrate that may have been reduced to nitrite, and the residue again dried on the steam bath. The zinc oxide is now in the form of zinc nitrate and may be separated from the sodium nitrate by either of the following methods:

1. The residue is dried at 110°–120° C. and weighed as $NaNO_3$ and $Zn(NO_3)_2$. It is then dissolved in water, the zinc precipitated with Na_2CO_3, filtered, ignited and weighed as ZnO, and the $NaNO_3$ taken by difference; the total $NaNO_3$ plus $Zn(NO_3)_2$ minus $(ZnO \times 2.33) = NaNO_3$.

2. The residue is gently heated over a burner until evolution of oxides of nitrogen from decomposition of the $Zn(NO_3)_2$ has ceased, and the remaining residue weighed as $NaNO_3$ and ZnO. It is then treated with water, the insoluble ZnO filtered on a Gooch crucible, ignited and weighed, the $NaNO_3$ being taken by difference.

Ammonium nitrate is determined in a separate portion of the water extract by the usual method of distillation and titration.

The sum of the amounts of NH_4NO_3, $NaNO_3$, and ZnO found will be somewhat less than the total water extract owing to the presence of water-soluble organic material from the carbonaceous absorbents.

Gelatin Dynamite

This is a form of nitroglycerin explosive in which the nitroglycerin, instead of being absorbed in porous materials such as wood pulp, is combined with nitrocellulose in the form of a gelatinous plastic mass. As little as 3.5% of suitable grade of nitrocellulose containing about 12% nitrogen will, when heated with nitroglycerin, at about 60° C., form a jelly-like non-fluid mass when cooled to ordinary temperature. " Blasting gelatin," used to a considerable extent where great explosive strength is required, is a stiff colloid composed of 90 to 93% nitroglycerin and 10 to 7% nitrocellulose.

All blasting explosives containing such colloids of nitroglycerin and nitrocellulose combined with an active " dope " or base, consisting of a nitrate and combustible material, are termed gelatin dynamites. This type of explosive is also known in some countries as " Gelignite."

Sampling.—Owing to its pasty consistency the sample of gelatin dynamite must be prepared by cutting portions of a number of cartridges into thin bits with an aluminum or platinum spatula. The use of a steel spatula or knife for this purpose is not to be recommended for reasons of safety. An ample quantity of sample thus prepared is well mixed and bottled. Owing to its tendency to again form a solid mass upon standing, it should be analyzed as soon as possible after being prepared.

Analysis.—The principle ingredients that may be found in the different types of gelatin dynamite are nitroglycerin; nitrocellulose; sulfur; rosin; sodium, potassium or ammonium nitrate; calcium or magnesium carbonate; wood pulp, cereal products and similar carbonaceous combustible materials. Low-freezing gelatins may also contain nitrotoluenes or other nitrosubstitution compounds, etc.

Moisture is determined as described for "straight" dynamite, and the extraction with ether made in the usual manner except that ether free from alcohol (distilled over sodium) is used in order to prevent partial solution of the nitrocellulose. The latter is readily soluble in a mixture of ether and alcohol, and as ordinary U. S. P. ether contains about 4% of alcohol, there is a possibility that an appreciable part of the 0.5% to 2.0% of nitrocellulose present in the sample will be dissolved unless pure ether is used. The ether extract is evaporated and analyzed as already described and the water extraction made in the usual manner. If more than 1 or 2% of sulfur was present it will not have been completely removed by the ether, unless the extraction was continued for a sufficiently long time. In this event, it is necessary to make an additional extraction with carbon disulfide in the Wiley apparatus subsequent to extraction with water.

Nitrocellulose.—After the extractions with ether, water, and CS_2 (if necessary) have been made, the nitrocellulose is determined, preferably by extraction with acetone, which is a better solvent for the purpose than a mixture of ether and alcohol. It is advisable to separate the dry residue from the crucible, leaving the asbestos mat intact if possible. The residue is transferred to a small beaker, covered with acetone and allowed to stand at least 3 or 4 hours with occasional stirring. It is then filtered through the original crucible, washed with acetone, dried and weighed, the loss of weight being regarded as nitrocellulose. To correct for small amounts of extract from the wood pulp or other carbonaceous material, the acetone solution may be evaporated to about 20–25 ml., and diluted gradually with a large volume (about 100 ml.) of hot water, which volatilizes the acetone, precipitating the nitrocellulose as a white flocculent mass, which is filtered, dried, and weighed.

The remainder of the analysis is conducted as for straight dynamite.

It will be found that the results of analysis of a gelatin dynamite do not agree with its trade markings. For example, the usual "40% strength" gelatin dynamite actually contains from 30 to 33% of nitroglycerin and about 1% of nitrocellulose. Weight for weight this explosive is considerably weaker than 40% straight dynamite, which contains 40% of nitroglycerin.

Low-Freezing Dynamite

Low-freezing dynamites vary from the dynamite types already discussed by containing an ingredient which reduces the freezing point of the nitroglycerin. This ingredient replaces a portion of the nitroglycerin which would be used in an equal grade of ordinary straight dynamite, ammonia dynamite, or gelatin dynamite. While straight nitroglycerin dynamite may freeze at temperatures as high as 8° C. (46° F.), some of the low-freezing dynamites freeze only at temperatures considerably below 0° C. Many of this type, however, cannot be relied upon to resist freezing at temperatures below the freezing point of water.

The additions made to nitroglycerin for this purpose include the nitrotoluenes, nitroxylenes, nitrohydrins, nitrosugar, nitropolyglycerin (tetranitrodiglycerin), and nitroglycol. Any of these substances present will be found in the ether extract together with, and in most cases dissolved in, the nitroglycerin.

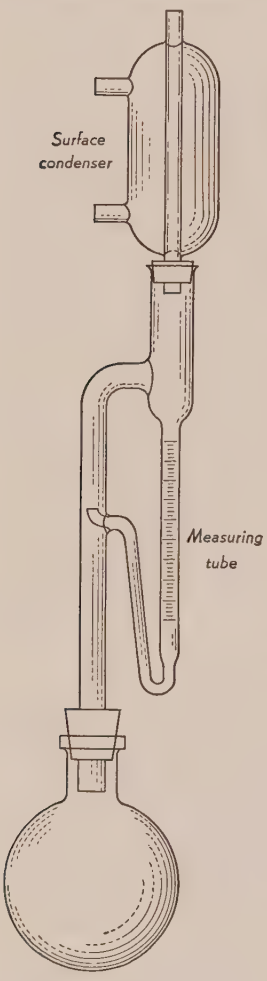


Fig. 237. Moisture Determination Apparatus for Dynamites, Oils, Fats, Waxes, Petroleum.

Moisture.—The determination of moisture may be carried out as already described for "straight" nitroglycerin dynamite (p. 1663), except when there are present such substances as nitroglycol or mononitrotoluene, whose volatility would prevent an accurate determination. An appreciable amount of nitroglycol, for example, would be lost in an attempt to desiccate to even approximately constant weight over sulfuric acid, even without vacuum. The loss of weight on desiccation should therefore be checked against the difference between the total loss on extraction with ether and the direct weight of the ether extract after evaporation of the ether in a bell-jar evaporator (p. 1664).

The following method for the determination of moisture especially in dynamites containing nitroglycol was developed by the Explosives Chemical Laboratory of the U. S. Bureau of Mines: 50 grams of the dynamite is weighed into a 500-ml. round bottom flask to which is attached a special moisture collecting tube. To the top of this tube is attached a small surface condenser. 150 to 200 ml. of carbon tetrachloride (free from H_2O) is added through the moisture collecting tube and the flask heated to boiling on a water bath for 1 hour. The CCl_4 and water volatilized are condensed and fall back into the measuring tube, the water separating on top of the CCl_4, while the excess of the latter runs back into the flask. The measuring tube is graduated in 0.1 ml. and the moisture is read direct. The tube should be standardized before use. The assembled apparatus is shown in Fig. 237.[5]

Nitrotoluenes.—Trinitrotoluene is not readily soluble in nitroglycerin and separates as crystals on evaporation of the ether from the ether extract, enabling it to be qualitatively separated and identified. It may be determined by difference, the nitroglycerin being determined by means of the nitrometer. Any dinitrotoluene present may also be determined in this manner together with the trinitrotoluene, but if mononitrotoluene is also

[5] A very similar method in which a solvent lighter than water is used, preferably benzene, is recommended for the determination of moisture in smokeless powders containing nitroglycerin, by F. Becker and P. Dittmar, Z. ges. Schiess-Sprengstoffwesen, **29**, 327, 371 (1934).

present, the determination of the nitrogen of the nitroglycerin will be slightly in error by about 0.5530 gram of nitroglycerin for every gram of mononitrotoluene present.[6]

Mononitrotoluene is, however, seldom present except as an impurity in the so-called liquid di- and trinitrotoluenes used in low freezing dynamites, so that the determination of the nitroglycerin is usually fairly accurate and the nitrotoluenes may be calculated by difference.

The total nitrogen of the combined nitroglycerin and nitrosubstitution compound may also be determined, the nitrogen of the nitroglycerin deducted and the amount of nitrosubstitution compound calculated from the resulting difference, if the identity of the nitrosubstitution compound has been established. A suitable modification of the Kjeldahl method which has been found applicable to difficultly decomposable nitrocompounds is as follows:[7] This method is, of course, applicable to mixtures containing nitroglycerin.

Modified Kjeldahl Method for Nitrogen.—About 0.5000 g. of the nitrocompound is weighed into a 500-ml. Kjeldahl flask, 30 ml. of 96% H_2SO_4 and 2 g. salicylic acid added and the sample dissolved by heating on a steam bath if necessary. Cool; add 2 g. zinc dust in small portions, with cooling and rotating the flask. Continue the shaking at 15 minute intervals for 2 hours and let stand overnight. Then heat over a small flame till fuming has ceased (about 2 hours), cool slightly and add 1 g. HgO and boil 1–1½ hours longer. Cool and add 7.5 g. K_2SO_4 and 10 ml. H_2SO_4 and boil 1½ to 2 hours more. If the solution is not clear and almost colorless, add 1 g. more K_2SO_4 and boil longer. Cool and add 250 ml. H_2O to dissolve the cake formed, then add 25 ml. K_2S solution (80 g. per liter H_2O), 1 g. granulated Zn, and 85–90 ml. NaOH solution (750 g. per liter H_2O), and distill as usual in the Kjeldahl determination, collecting the NH_3 in standard H_2SO_4 solution. A blank determination without sample is advisable.

Separation of Nitrocompounds from Nitroglycerin.—Hyde has devised a satisfactory method for actual separation of nitrosubstitution compounds from nitroglycerin, depending on the differences in solubility of these ingredients in carbon bisulfide and dilute acetic acid.[8] Nitroglycerin is only slightly soluble in CS_2, but readily soluble in dilute acetic acid, while most nitrocompounds are much more soluble in CS_2 and much less soluble in dilute acetic acid than nitroglycerin. CS_2 and acetic acid are only slightly miscible. Hence nitroglycerin and a nitrocompound may be partly separated by shaking the mixture with CS_2 and dilute acetic acid, allowing the two solvents to separate into two layers and drawing off one of the layers. The CS_2 layer will contain most of the nitrocompound and the acetic acid layer most of the nitroglycerin.

[6] Storm, C. G., "The Effect of Nitrotoluenes on the Determination of Nitroglycerin by Means of the Nitrometer," Proc. 8th Int. Cong. Appl. Chem., Vol. 4, 1912, p. 117; also Bur. of Mines Bull. 41, p. 62, 1913.

[7] Cope, W. C., "Kjeldahl Modification for Determination of Nitrogen in Nitrosubstitution Compounds," J. Ind. and Eng. Chem., **8**, 592 (1916). See also Cope, W. C., and Taylor, G. B., "The Determination of Nitrogen in Substances Used in Explosives," Tech. Paper 160, Bur. of Mines, 1917.

[8] Hyde, A. L., "The Quantitative Separation of Nitrosubstitution Compounds from Nitroglycerin," J. Am. Chem. Soc., **35**, 1173 (1913). (See also Bur. Mines Bulletin 96, pp. 47–50, 1916.)

Hyde's method involves a continuous fractional extraction in a rather complicated apparatus consisting of 13 long narrow extraction tubes, connected with each other and with a condenser, reservoir and distilling flask so as to form a closed circulating system, the CS_2 continually passing in a train of fine drops through acetic acid in the series of extraction tubes, carrying with it the nitrocompound, the nitroglycerin tending to remain dissolved in the acetic acid. Practically a complete separation is finally obtained, the nitrocompound dissolved in the CS_2 collecting in the distilling flask at the end of the extraction train and the nitroglycerin remaining in solution in the acetic acid in the tubes. The CS_2 is evaporated and the nitrocompound weighed. Reference should be made to the original article by Hyde for details as to construction and operation of the apparatus.

Nitrosugars.—The nitrates of sugar, improperly called nitrosugar, are used to a considerable extent for lowering the freezing point of nitroglycerin. This substance is soluble in nitroglycerin, being prepared with the latter by nitrating a solution of cane-sugar in glycerin, and no method is known for its separation from nitroglycerin. Hoffman and Hawse [9] have reported on an optical method for the determination of nitrated sugar in nitroglycerin mixtures, based on the use of the polariscope. As an example of the application of the method, 10.65 g. of a nitrated mixture of glycerin and sugar was dissolved in 100 ml. alcohol and its angle of rotation found to be $a = 3.07°$. The specific rotatory power of sucrose octanitrate having been determined as $\alpha = 56.66$, the formula: C (concentration) $= a/2\alpha$ gives a result of 25.44% sucrose octanitrate in the sample.

The result of the optical method may be roughly checked by a determination of the total nitrogen of the combined nitroglycerin and nitrosugar, assuming the nitrogen content of the nitrosugar to be 15% (theoretical for sucrose octanitrate 15.95%), and that of nitroglycerin 18.50%.

Nitrochlorhydrins.—Dinitromonochlorhydrin has been known for years as a partial substitute for nitroglycerin in explosives. It is a solvent for nitrocellulose in smokeless powders and has an appreciable effect in lowering the freezing point of nitroglycerin. Some years ago it came into use in this country as a substitute for nitrotoluenes in low freezing dynamites.

A mixture of dinitrochlorhydrin and nitroglycerin will have a lower nitrogen content than pure nitroglycerin, the dinitrochlorhydrin containing only 14.0% N, as compared with 18.50% N in nitroglycerin. The dinitrochlorhydrin may be readily identified and determined quantitatively by treating the mixture containing this substance and nitroglycerin with an excess of alcoholic solution of KOH, heating on the steam bath until saponification is complete, and determining the chlorine in the solution as chloride.

It must be noted that dinitrochlorhydrin is somewhat more volatile than nitroglycerin and therefore in evaporating the ether from the ether extract it is advisable to make use of the bell-jar evaporator (p. 1664) so as to minimize its loss during evaporation.

Nitropolyglycerin.—Nitrated polymerized glycerin—usually a mixture of tetranitrodiglycerin and trinitroglycerin—is sometimes found in low-freezing explosives. This mixture will show a lower N-content than nitroglycerin,

[9] Hoffman, E. J. and Hawse, V. P., "The Nitration of Sucrose Octanitrate," J. Am. Chem. Soc., **41**, 235–247 (1919).

since pure tetranitrodiglycerin contains only 16.19% N. The presence of the latter substance is indicated by low solubility in dilute acetic acid (60 volumes glacial acetic acid to 40 volumes water). One gram of nitroglycerin dissolves in about 10.5 ml. of this acid, while 1 gram of a mixture containing 82.25% tetranitrodiglycerin required 120 ml. of the acetic acid to completely dissolve it. In dissolving such a mixture, it will be found that a part of the mixture dissolves more readily than the remainder. If the more difficultly soluble portion is separated, dried in a desiccator and its nitrogen content determined in the nitrometer, it will be found to contain a much lower % N than the original mixture, approximating the figure for tetranitrodiglycerin, 16.19% (an actual trial gave 16.24% N).

If the presence of tetranitrodiglycerin is established by the above procedure and no other substances except nitroglycerin are present, the proportions of these two ingredients in the ether extract may be readily calculated from the N-content as found by the nitrometer.

Nitroglycol.—Ethylene glycol dinitrate (commonly called nitroglycol) is rather extensively used at present for lowering the freezing point of nitroglycerin explosives. The usual procedure is to nitrate a mixture of glycerin and glycol. The product has substantially the same nitrogen content as nitroglycerin, the chief distinguishing characteristic being volatility—nitroglycol having a considerably higher vapor pressure. A continual loss of weight in evaporating the ether extract may therefore serve as an indication of the presence of nitroglycol.

"PERMISSIBLE" EXPLOSIVES

"Permissible" explosives are coal mining explosives which have passed the prescribed tests of the Bureau of Mines and are recommended by the Bureau for use in gassy and dusty mines. Their important characteristic is a relatively low flame temperature, which is brought about by modifying the composition of the usual types of dynamites and other blasting explosives. The general methods of reducing the flame temperature of explosives [10] are summarized as follows:

(*a*) Addition of an excess of carbon—forming less CO_2 and more CO in the gases of explosion.
(*b*) Addition of free water or of solids with water of crystallization.
(*c*) Addition of inert materials.
(*d*) Addition of volatile salts.

[10] The thermochemical considerations involved are discussed in Bureau of Mines Bulletin No. 15, "Investigations of Explosives Used in Coal Mines," 1912, and the details of analysis in Bureau of Mines Bulletin No. 96, "The Analysis of Permissible Explosives," C. G. Storm, 1916.

The analysis of explosives of this class is therefore generally more complicated than that of the ordinary types of blasting explosives because of the greater variety of ingredients used in manufacture. A partial list of substances which have been found in low-flame explosives manufactured in this country is shown below, arranged according to their solubility in the general scheme of analysis:

Soluble in Ether	*Soluble in Water*	*Soluble in Acids*
Nitroglycerin	Ammonium nitrate	Aluminum
Nitropolyglycerin	" chloride	Calcium carbonate
Nitrotoluenes	" sulfate	" silicide
Nitrosugars	" oxalate	Ferric oxide
Nitrochlorhydrins	" perchlorate	Magnesium carbonate
Nitroglycol	Alum (cryst.)	Zinc
Paraffin	Aluminum sulfate (cryst.)	Zinc oxide
Resins	Barium nitrate	
Sulfur	Calcium sulfate (cryst.)	
Vaseline	Gums	
Oils	Magnesium sulfate (cryst.)	
	Potassium chlorate	
	" nitrate	
	" perchlorate	
	Sodium nitrate	
	" chloride	
	" bicarbonate	
	" carbonate	
	Sugar	
	Zinc oxide	

Insoluble

Charcoal	Peanut shell meal
Clay	Powdered slate
Coal	Rice hulls
Corn meal	Sawdust
Corncob meal	Turmeric
Kieselguhr	Vegetable ivory meal
Nitrocellulose	Wheat flour
Nitrostarch	Wood pulp
Nitrated wood	

Qualitative Analysis.—The qualitative examination of a " permissible " explosive is conducted in the same manner as has been described for dynamite (see page 1662), and, in view of the greater variety of constituents that may be present, is quite essential before a suitable scheme for quantitative separation can be chosen.

Tests for some of the more unusual substances not generally found in the ordinary types of blasting explosives, and not already discussed under " Low-freezing Explosives," are made as follows:

Test for Sugar.—The presence of water-soluble organic substances is indicated by an appreciable charring of the residue obtained by evaporating a portion of the water extract to dryness and then heating gradually over a burner. A slight charring may result from water-soluble portions of cereal products, wood-pulp, etc., and may be disregarded. Sugar is identified by acidifying some of the water solution with a little dilute HCl, heating to boiling, neutralizing with KOH and then boiling with Fehling's solution. A precipitation of cuprous oxide indicates the presence of sugar.

Test for Gum Arabic.—Gum arabic is precipitated by the addition of a solution of basic lead acetate to the water extract, a white, flocculent precipitate of indefinite composition resulting (see Determination of Gum Arabic, p. 1677).

Test for Nitrostarch.—Nitrostarch is best identified by microscopic examination of the residue insoluble in water. It is easily distinguished from unnitrated starch by means of a solution of iodine in KI, which colors the starch granules dark blue but does not affect the granules of nitrostarch.

Test for Chlorides, Chlorates, and Perchlorates.—These three substances present in a solution may be identified as follows: Acidify slightly with nitric acid, add excess of $AgNO_3$, heat to boiling, shake well, and filter off the silver chloride. To the filtrate add a few ml. of 40% solution of formaldehyde (formalin), and boil to reduce chlorates to chlorides. This reduction is best carried out by heating on the steam bath for about an hour. Any chloride thus formed is then separated by further precipitation with $AgNO_3$ and removed by filtration. The filtrate is then evaporated to dryness, the residue transferred to a crucible and fused with dry Na_2CO_3. The fused mass is treated with dilute HNO_3, when the presence of perchlorate will be indicated by an insoluble precipitate of AgCl.

Mechanical Separation of Solid Igredients.—It is frequently of advantage, especially in connection with the interpretation of the results of analysis of an explosive mixture containing a number of water-soluble salts, to determine the identity of one or more of the components of the mixture by means of screening or by a method of separation depending on variation in specific gravity of the components. Such methods are facilitated by the fact that the ingredients of blasting explosives are frequently not finely pulverized in the course of manufacture.

(*a*) *By Screening.*—25 to 50 grams of the sample is washed several times with ether to remove nitroglycerin and ingredients of an oily nature, the solid residue dried to remove adhering ether and then sifted through a set of sieves. An examination of the portions held by the 10- and 20-mesh screens will usually show the presence of coarse crystals which are large enough to be sorted out with the aid of forceps, submitted to qualitative tests and identified with certainty. A single crystal may sometimes be identified by dissolving it in a drop of water on a microscope slide, allowing the water to evaporate and examining the resulting crystals under the microscope. The writer has frequently identified three or four ingredients of an explosive in this manner.

(*b*) *By Specific Gravity Separations.*—This method, applied to the analysis of explosives by Storm and Hyde,[11] depends on the separation of solids from a mixture by means of inert liquids of different specific gravities. A series of mixtures of chloroform (sp.gr. 1.49) and bromoform (sp.gr. 2.83) is prepared covering as wide a range of specific gravity as may seem desirable. Portions of the dried sample previously extracted with ether as in (*a*) are added to such liquid mixtures and the heavier salts, which settle to the bottom, separated from the lighter ones. For example a mixture of ammonium nitrate (sp.gr. 1.74) and sodium chloride (sp.gr. 2.17) is readily separated into its components in a liquid with a specific gravity of (*e.g.*), 1.90, so that the components can be tested separately and the analyst assured that the mixture is not composed

[11] Storm, C. G., and Hyde, A. L., "Specific Gravity Separation Applied to the Analysis of Mining Explosives," Tech. Paper No. 78, Bureau of Mines, 1914.

of sodium nitrate and ammonium chloride—which could not be ascertained by ordinary quantitative analysis. (For example, a mixture composed of 16.61% Na, 44.76% NO_3, 13.00% NH_4 and 25.63% Cl may contain either 61.37% $NaNO_3$ and 38.63% NH_4Cl, or 57.76% NH_4NO_3 and 42.24% NaCl, or varying proportions of all four ingredients.) The chloroform-bromoform mixtures are recovered by filtering and used repeatedly.

The specific gravities of some of the more common salts that may be found are as follows:

Ammonium alum (cryst.)	1.62
" chloride	1.52
" nitrate	1.74
" perchlorate	1.87
" sulfate	1.77
Barium nitrate	3.23
Calcium carbonate (ppt'd)	2.72
" sulfate (anhydrous)	2.97
" sulfate+$2H_2O$	2.32
Magnesium carbonate	3.04
" sulfate+$7H_2O$	1.68
Manganese dioxide	5.03
Potassium alum (cryst.)	1.75
" chlorate	2.33
" chloride	1.99
" nitrate	2.09
" perchlorate	2.52
" sulfate	2.66
Sodium chloride	2.17
" nitrate	2.26
" sulfate (anhydrous)	2.66
" sulfate+$10H_2O$	1.46

Moisture.—The determination of moisture in all types of " permissible " explosives is carried out by the method described for nitroglycerin dynamites (page 1663). The influence of the slight volatility of nitroglycerin and of certain nitrosubstitution compounds on the results of this determination has been discussed (pp. 1664, 1670). A more serious factor in the case of many " permissible " explosives is the presence of salts containing water of crystallization. Most salts of this type (*e.g.*, $MgSO_4 \cdot 7H_2O$) undergo a gradual loss of a large part of their combined water on desiccation over either H_2SO_4 or $CaCl_2$, thus rendering it impossible to differentiate between hygroscopic moisture and combined water. Attempts to remove the total water content by heating at a temperature high enough to drive off all of the water of crystallization are useless on account of the increased volatilization of nitroglycerin, ammonium nitrate, etc., at such temperatures.

In such cases it is necessary to determine all other constituents by direct methods and estimate moisture by difference, the salt to which the water of crystallization belongs being calculated as containing its full quota of water; or the crystallized salt may be calculated as anhydrous and the difference from 100% reported as " water of crystallization plus moisture."

Extraction with Ether.—The extraction with ether, the evaporation of the ether, and the analysis of the ether-soluble portion are conducted as already discussed for nitroglycerin dynamites (pp. 1664, 1665).

In drying the crucibles containing the residue insoluble in ether, a temperature of 100° C. may be used except when the residue contains ammonium nitrate or organic nitrates such as nitrocellulose, nitrostarch, or nitrated wood. When any of these substances are present, the residue should be dried to constant weight at 70° C. Except when salts containing water of crystallization are present, the amount of ether-soluble material found is calculated by deducting the moisture determined by desiccation, from the difference between the weight of original sample and the weight of the dried residue insoluble in ether. The procedure followed when water of crystallization is present is noted in the preceding paragraph.

Extraction with Water.—Water-soluble salts are extracted from the weighed residue insoluble in ether as already described, the residue left in the crucibles dried to constant weight at 95 to 100° C., cooled and weighed. The water soluble salts in the solution are determined by the usual methods of inorganic analysis.

Nitrates.—In determining nitrates by the nitrometer method (see p. 1666) it must be remembered that the presence of a considerable quantity of chlorides may interfere with the accuracy of the results. Many of the " permissible " explosives contain sodium chloride in amounts varying from 1% to 10 or 15%. M. T. Sanders [12] has shown that if the sodium chloride is present in an amount exceeding 15–17% of the sodium nitrate, the result is not accurate within 0.1%. Smaller amounts of sodium chloride do not interfere, except to increase the amount of sludge formed in the nitrometer.

Nitrates may also be determined by the " nitron " method of Busch.[13]

Chlorates.—Chlorates may be determined by any of the methods described on page 274 (reduction with SO_2, $FeSO_4$, or Zn) or by the formaldehyde method.[14] In the latter method a portion of the solution, containing about 0.5 g. of chlorate, is diluted to 150 ml., 5–10 ml. of 40% formaldehyde solution, 2 ml. dilute HNO_3 (1 : 3), and 50 ml. of approx. tenth normal silver nitrate added, the solution covered and heated on the steam bath for about 4 hours, when the precipitate of AgCl is filtered off, washed, dried and weighed. This method is accurate to .05 to .10%.

Perchlorates.—The determination of perchlorates by reduction to chlorides on ignition with NH_4Cl in the presence of platinum is described on page 275. Perchlorates may also be determined by means of precipitation with " nitron " in exactly the same manner as for nitrates. The weight of nitron perchlorate ($C_{20}H_{16}N_4HClO_4$) found, multiplied by 117.5 (mol. wt. of NH_4ClO_4) and divided by 412.5 (mol. wt. of nitronperchlorate), gives the weight of perchlorate found, expressed as NH_4ClO_4.

Gum Arabic.—This substance, sometimes used as a binder in dry explosive mixtures—especially chlorate or perchlorate powders—is determined by precipitation with basic lead acetate solution, prepared by adding 150 g. of normal lead acetate and 50 g. lead oxide (PbO) to 500 ml. distilled water, heating

[12] Sanders, M. T., "The Effect of Chlorides on the Nitrometer Determination of Nitrates," J. Ind. and Eng. Chem., **12**, 169–170 (1919).

[13] See page 639, also, for further details, "The Analysis of Permissible Explosives," Bureau of Mines, Bulletin 96, pages 60–62.

[14] Storm, C. G., "The Analysis of Permissible Explosives," Bulletin 96, Bureau of Mines, pp. 63–64, 1916.

almost to boiling, and filtering. This reagent is added to the solution containing the gum arabic until no further precipitation occurs; the mixture is allowed to stand for several hours, then filtered, washed with absolute alcohol, dried at 100° C. and weighed. The weight of precipitate multiplied by the factor 0.4971 (determined experimentally) gives the weight of gum arabic found. Chlorides or sulfates, if present, interfere with the determination and must be first removed.

Sugar.—Sugar may be present as an ingredient in some " permissible " explosives, and is always found in small amounts in the water extract if cereal products such as corn meal or wheat middlings are present. A portion of the water extract is acidified with HCl (1 ml. conc. HCl to 100 ml. solution), heated just to boiling, cooled, nearly neutralized with Na_2CO_3, an excess of Fehling's solution added and the mixture heated until reduction is complete. The Cu_2O is filtered from the blue liquid, dried, ignited to constant weight, and weighed as CuO. This weight $\times 0.4308$ equals weight of cane sugar. The result is corrected for the result of a blank determination using distilled water instead of the water extract. By the use of this method after first extracting with ether, then with water, corn meal was found to contain 2.65% and wheat middlings 6.25–7.00% of sugar. Thus an explosive containing 25% wheat middlings would show as much as 1.75% of sugar in its water extract.

Extraction with Acid.—As in the ordinary nitroglycerin dynamites, the substances removed from " permissible " explosives by acid extraction are chiefly substances added as antacids, including calcium carbonate, magnesium carbonate and zinc oxide. Other acid-soluble materials that may be present include metallic aluminum or zinc, ferric oxide, manganese dioxide, and calcium silicide. When starch is present, the residue from the water extraction is subjected to hydrolysis in boiling dilute HCl as already described (page 1667), and the acid-soluble inorganic components determined in the filtrate by the usual methods. An extraction with cold acid is made only when there is no starch present.

Extraction with Acetone: Nitrocellulose and Nitrostarch.—If either nitrocellulose or nitrostarch is present, an extraction with acetone is made as described for gelatin dynamite (page 1669). It should be noted in connection with the preceding steps in the analysis that in order to avoid partial solution of these substances in ether, the ether used in the ether extraction should be alcohol-free (distilled from sodium), and also that all drying of residues containing these materials should preferably be conducted at 70° C. instead of 100° C., in order to avoid partial decomposition. It is impracticable to separate nitrostarch from nitrocellulose but they are not likely to be found together in the same explosive. Small amounts of nitrocellulose are detected less readily than nitrostarch, which is easily identified by the microscope.

Insoluble Residue and Ash.—The insoluble residue is usually carbonaceous combustible or absorbent material and is in most cases readily identified by means of a microscope (preferably binocular) with low power (25–50 diameters). The possible presence of any inorganic material which may have been overlooked in the analysis is detected by means of a determination of ash, the residue being ignited until all carbon is burned off and the mineral residue weighed. This is usually not over 0.2%. If higher than 0.5%, there is reason

to suspect that some such material as kieselguhr or clay is present, or that the extractions with water or acid were not complete.

NITROSTARCH EXPLOSIVES

General Nature.—Nitrostarch explosives have been for a number of years used to a very considerable extent in this country for commercial blasting purposes, chiefly for quarrying. During the war, explosives of this class were adopted by the United States for certain military purposes and proved satisfactory substitutes for trinitrotoluene as bursting charges for hand grenades, rifle grenades and trench mortar shell.

The commercial nitrostarch explosives may contain, in addition to the nitrostarch, any or all of the following components: oxidizing agents, as sodium or ammonium nitrates, combustible material, such as charcoal, flour, sulfur, etc., mineral oil, and antacids, such as calcium carbonate, or zinc oxide. Nitrostarch military explosives may consist of some such mixture as the above, or may be composed almost entirely of nitrostarch with the addition of relatively small amounts of oils and materials used for granulating. Some types of nitrostarch explosives proposed for military use contained water in amounts up to 10–15% combined with a mixture of nitrostarch and a soluble nitrate.

For commercial use, nitrostarch explosives are put up in cartridge form in paper wrappers, just as nitroglycerin explosives are prepared.

Moisture.—Moisture is determined as in the case of nitroglycerin dynamites. 3 to 5 grams of the sample is desiccated over sulfuric acid for 2–3 days (2 days is usually sufficient to give constant weight), or for 24 hours in a vacuum desiccator with a vacuum of at least 700 mm. of mercury. Unlike nitroglycerin, nitrostarch does not volatilize and may be desiccated to constant weight. When heated to higher temperatures, *e.g.*, 100° C., for any extended time, it undergoes, like all nitric esters, a gradual decomposition with loss of weight.

Extraction with Petroleum Ether: Oils, Sulfur, etc.—The small amount of alcohol usually present in ordinary grades of ethyl ether, is sufficient to cause partial solution of the nitrostarch, if ethyl ether is used for removing oily ingredients, sulfur, etc., nitrostarch being readily soluble in mixtures of ether and alcohol. It is therefore advisable to use petroleum ether, which does not dissolve nitrostarch, for this extraction.

A sample of about 10 grams of the explosive, in a Gooch crucible with asbestos mat, is extracted with pure petroleum ether of about 0.65 specific gravity, the excess solvent removed by suction and the crucible with sample dried to constant weight at approximately 70° C. The % loss of weight, minus the moisture content, already determined, represents the percentage of ether-soluble material present. The petroleum ether is removed by evap-

oration, the residue of ether-soluble materials dried, weighed, and its components determined by the methods used for dynamites.

Extraction with Water: Nitrates, Gums, etc.—The dried and weighed residue insoluble in petroleum ether is extracted with distilled water to remove the nitrates or other water-soluble materials. The insoluble residue left in the crucible is dried at a temperature of 80° C. (100° may cause some decomposition of the nitrostarch) for several hours, and weighed, the loss of weight being total water extract and serving as a check against the sum of the components separately determined.

Ammonium nitrate, if present, is determined in the water solution by the usual method of distillation of the NH_3 after adding an excess of alkali. Sodium nitrate is determined by evaporating the water extract, volatilizing ammonium salts, and weighing the residue after re-oxidizing with nitric acid if charring has indicated the presence of any water-soluble organic material (page 1667).

If the original explosive is granular in form, the presence of a binding or agglutinating material in the water extract may be suspected. Although numerous other substances may be used for the purpose, gum arabic is frequently employed as a binding agent in different types of dry explosives. A qualitative test for gum arabic has been mentioned on page 1675, and its quantitative determination may be conducted as described on page 1677, by precipitation with basic lead acetate solution.

Insoluble Residue: Nitrostarch, Charcoal, Cereal Products, etc. *Starch.*—A microscopic examination of the weighed insoluble residue will usually serve to identify its components. Any un-nitrated starch or cereal product is readily distinguished from nitrostarch by treating with a drop of KI solution of iodine and examining under the microscope, when the un-nitrated starch granules will appear blue or black and the nitrated starch colorless or yellow. Charcoal is identified by its color.

Un-nitrated starch, if present in an amount greater than a trace, is determined by boiling with dilute H_2SO_4 or HCl until iodine solution no longer colors a drop of the liquid blue, then filtering and washing thoroughly. The residue is dried at 80° C. and weighed, the loss of weight representing starch.

Nitrostarch.—Another portion of the insoluble residue (the analysis being conducted in duplicate) is extracted with acetone in a Wiley extractor or other continuous extraction apparatus, or by transferring the residue from the crucible to a small beaker, digesting in acetone with stirring, and filtering through the same crucible, washing with fresh acetone. This extraction dissolves all of the nitrostarch, leaving any charcoal or cereal products that may be present. The residue is dried at 100° C. and weighed, the loss of weight representing nitrostarch.

The nitrogen content of the nitrostarch may be determined, if desired, by precipitating the nitrostarch from the clear acetone solution by the addition of water and evaporation on a steam bath. A portion of the white, floury precipitate is then dried at 70°–80° C., weighed, and its nitrogen content determined in the nitrometer (see page 650, Vol. I).

Charcoal.—If charcoal is present its weight may be taken direct, in the absence of cereal products or other substances. When the residue contains cereal products, the material left after hydrolysis of the starch and extraction

of the nitrostarch will contain the crude fibre of the cereal together with charcoal or other insoluble ingredients. A separation of such components is usually impracticable.

Trinitrotoluene (TNT)

Trinitrotoluene, commonly designated in this country by the abbreviation TNT, is also known in this and other countries by such names as triton, trotyl, tolite, trilite, trinol, tritolo, etc. The term trinitrotoluol, which is probably more commonly used than trinitrotoluene, is incorrect according to approved chemical nomenclature.

This explosive is of the greatest importance as a high explosive for military use, being adaptable as a bursting charge for high explosive shell, trench mortar shell, drop-bombs, grenades, etc., because of its powerful explosive properties, relative safety in manufacture, handling, etc., its stability, its lack of hygroscopicity, and absence of any tendency to form sensitive compounds with metals.

It is classified by the Ordnance Department, U. S. A., into two grades, according to purity—Grade I with solidification point of at least 80.2° C. and Grade II with solidification point of at least 76.0° C. Other requirements, the same for both grades, are as follows: acidity (as H_2SO_4), not more than 0.01%; insoluble in benzene or 95% alcohol, not more than 0.10%; moisture, not more than 0.10%. Grade I represents material purified by means of sodium sulfite.

Solidification Point.—The determination of the solidification point or "setting point" of TNT is the best single test for purity of this compound, and is preferably carried out as follows:

A sample of about 50 grams of TNT is placed in a 1″×6″ test tube and melted by placing the tube in an oven at about 95° C. The tube is then inserted through a large cork stopper into a larger test tube about 1½″×7″, which, in turn, is lowered into a wide-mouth liter bottle, so that the rim of the large tube rests on the neck of the bottle. The inner test tube is provided with a cork stopper containing 3 openings—one for a standard thermometer graduated in 1/10° C., one for a short thermometer which is passed just through the stopper and is used for noting the average temperature of the exposed mercury column of the standard thermometer, and the third opening being a small v-shaped notch at the side of the stopper, through which passes a wire whose lower end is bent in a loop at right angles to the axis of the tube and which is used for stirring the molten sample of TNT.

The standard thermometer is so adjusted that its bulb is in the center of the molten mass, and the stirrer is operated vigorously, the thermometer being watched carefully as the temperature falls. The temperature will finally remain constant for an appreciable time and then rise slightly, owing to the heat of crystallization of the TNT. As this point is reached, readings should be taken about every 15 seconds until the maximum temperature of the rise is reached. This temperature will usually remain constant for several minutes while crystallization is proceeding. The maximum reading, corrected for the emergent stem of the thermometer, is taken as the solidification point of the sample.

Ash.—About 5 grams of TNT is moistened with sulfuric acid and burned in a tared crucible. The residue is again moistened with a few drops of nitric acid and sulfuric acid and again ignited and the resulting ash weighed.

Moisture.—A sample of about 5 grams spread on a watch glass is desiccated over sulfuric acid to constant weight.

Insoluble.—A sample of about 10 grams is treated with 150 ml. of benzene or 95% alcohol, heated to boiling, and filtered while hot through a tared Gooch crucible with asbestos mat. The insoluble residue is washed with additional solvent, dried at 100° C. and weighed.

Acidity.—A 10-gram sample is melted in a large test tube or a flask and shaken with 100 ml. of neutralized boiling water, cooled and the water decanted. A similar treatment is given using 50 ml. of boiling water, the two portions of water combined, cooled and titrated with tenth normal NaOH, using phenolphthalein indicator. The acidity is calculated as % H_2SO_4 in the original sample.

Nitrogen.—Nitrogen is not usually determined in the inspection of TNT but when necessary it may be determined by the Dumas combustion method or the modification of the Kjeldahl method described on page 1671.

Picric Acid

Ordnance Department, U. S. A., specifications for picric acid prescribe that it shall have a solidification point of not less than 120° C.; that it shall contain not more than the following amounts of impurities:

Moisture—0.2% for dry material	22.0% for wet
Sulfuric acid (free and combined)	0.10%
Ash	0.2%
Insoluble in water	0.2%
Soluble lead	0.0004%
Nitric acid (free)	none

Solidification Point.—Dry the sample at a temperature not exceeding 50° C. Melt sufficient to give a 3-inch column in a 6-inch × ¾-inch test tube immersed in a bath of glycerin heated to 130° C. When the sample is completely melted remove the tube from the bath and stir the sample with a standardized thermometer graduated in 0.10 degrees, until the picric acid solidifies. During solidification the temperature will remain constant for a short time and then undergo a slight rise. The highest temperature reached on this rise is recorded as the solidification point. The test may be more accurately carried out using the apparatus and method as described under trinitrotoluene (p. 1681).

Moisture.—A weighed sample of about 10 grams is spread evenly on a tared watch glass and dried to constant weight (about 3–4 hours) at 70° C.

Sulfuric Acid.—About 10 grams is weighed and dissolved in 250 ml. of boiled distilled H_2O, acidified with HCl and heated to about boiling. Hot $BaCl_2$ solution is added with stirring and the mixture allowed to stand at least 1 hour on the steam bath. Filter hot on a tared Gooch crucible, wash with water, dry at 100° C. and weigh. Calculate $BaSO_4$ found as H_2SO_4 in original sample.

Ash.—About 5 grams is weighed in a crucible, moistened with sulfuric acid, burned carefully, and the residue ignited to burn off all carbon. The resulting ash is cooled and weighed.

Insoluble in Water.—10 grams of the sample is treated with 150 ml. boiling distilled water, boiled for 10 minutes, filtered while hot through a tared Gooch

crucible, washed well with hot water, and the insoluble residue on the filter dried at 100°, cooled, and weighed.

Soluble Lead.—The presence of soluble lead in picric acid is highly objectionable, because lead picrate is an extremely sensitive explosive and its presence would greatly increase the dangers involved in handling and loading picric acid. A weighed sample of about 300 g. is digested in a 2-liter flask with 100 ml. of a hot saturated solution of barium hydroxide in 65% alcohol. 1400 ml. of 95% alcohol is then added and the digestion continued at a temperature below the boiling point (with reflux condenser), until everything except traces of insoluble matter is in solution. The picric acid is then allowed to crystallize on cooling, and the solution filtered off, decanting the clear liquid from the crystals until 500 ml. of filtrate is obtained. This 500 ml., representing 100 g. of picric acid, is treated with 5 drops HNO_3 and 10 ml. of 0.1% $HgCl_2$ solution, and H_2S passed through it for 15 minutes. Allow the precipitate to settle for 20 minutes, filter and wash with alcohol saturated with H_2S. Dry and ignite the precipitate, then dissolve the residue in 9 ml. of HNO_3 (sp.gr. 1.42) by warming, add warm water to bring the volume to 50 ml., and electrolize at 0.4 ampere and 2.5 volts, temperature 65° C., for 1 hour. Wash the electrode by replacing the beaker with another one containing distilled water without interrupting the current. Dry and weigh the previously tared anode. The weight of lead peroxide found $\times 0.8661$ gives the percentage of soluble lead found.

Nitric Acid.—No coloration should result when a water solution of picric acid is treated with a solution of diphenylamine in sulfuric acid.

Ammonium Picrate

Ammonium picrate, also known in this country as "Explosive D," is of importance as a military explosive more on account of its insensitiveness to shock and friction, than because of its explosive strength, which is less than that of TNT. Its chief use is as a bursting charge in armor-piercing projectiles.

Military specifications require it to be prepared from picric acid of standard purity, to contain not less than 5.64% ammoniacal nitrogen, and not more than the following amounts of impurities:

Moisture	0.20%
Insoluble material	0.20%
Ash	0.20%
Free ammonia (NH_3)	0.025%
Free picric acid	0.025%

Moisture.—A sample of about 10 grams spread on a tared watch glass is dried at 95° C. to constant weight (about 2 hours).

Insoluble Material.—A 10-gram sample is boiled with 150 ml. of water for 10 minutes, filtered on a Gooch crucible, the residue washed with hot water, dried at 100° C. and weighed.

Ash.—A sample of about 1 gram is saturated with melted paraffin and burned in a tared crucible, the residue ignited to burn off all carbon, and the ash weighed.

Free Ammonia or Free Picric Acid.—A sample of about 5 grams is ground in a porcelain mortar with successive 50 ml. portions of water until the sample is entirely dissolved, each portion of the water being poured through a filter into

a 500-ml. Erlenmeyer flask. Add 3 to 5 drops of a saturated solution of sodium alizarin sulfonate or of a 1% alcoholic solution of methyl red and note whether the solution is acid or alkaline. Both indicators are yellow when acid. In alkaline solutions sodium alizarin sulfonate is purple and methyl red is red. Titrate the solution with N/10 acid or alkali. Subtract one drop from the volume used to allow for the amount required to convert the solution from neutrality to acidity or alkalinity. Calculate as follows:

$$\% \text{ free ammonia} = \frac{A \times 0.17B}{W},$$

$$\% \text{ free picric acid} = \frac{A \times 2.29B}{W},$$

where A = ml. N/10 solution used,
B = normality factor of solution,
W = weight of sample used.

Tetryl

Tetryl is the commercial term applied to the explosive trinitrophenylmethylnitramine, also improperly called tetranitromethylaniline. Its chief use is as a "booster" charge in high explosive shell, where it serves to transmit the detonating wave from the detonator or fuze to the less sensitive bursting charge. Being in immediate contact with the fuze it must be of a high degree of purity, and is required by Ordnance Department specifications to have a melting point of at least 128.5° C. and to contain not more than the following amounts of impurities:

Moisture	0.10%
Insoluble in Benzene	0.40%
Acidity (as H_2SO_4)	0.10%

Melting Point.—The sample to be used for this test is dried overnight in a vacuum desiccator or 2 hours at 95°–100° C .and pulverized to pass a 100-mesh screen. A capillary melting-point tube is filled to about ¼ inch from the bottom and attached to the stem of a standard thermometer so that the sample is next to the center of the bulb. The bath is properly agitated and provision made for correcting for the emergent stem of the thermometer. The temperature of the bath is raised rapidly to 120° C., then at the rate of 1° in 3 minutes, the temperature at which the first meniscus appears across the capillary tube being noted as the melting point.

Moisture.—A sample of about 5 grams is weighed in a wide shallow weighing bottle and dried over sulfuric acid in a desiccator for 48 hours, the sample being spread uniformly so that its depth is not over 0.5 cm. The loss of weight is regarded as moisture.

Insoluble in Benzene.—5 grams of sample is dissolved in 75 ml. of benzene, filtered through a tared Gooch crucible, and the residue washed with three 25-ml. portions of acetone, dried to constant weight at 100° C. and weighed.

Acidity.—The benzene filtrate from the determination of insoluble material is shaken with 100 ml. cold boiled distilled water in a separatory funnel, the water layer removed and the benzene solution given a second extraction with 50 ml. more water. The combined water extracts are titrated with N/20 NaOH solution, using phenolphthalein indicator.

Mercury Fulminate

In commercial blasting caps and electric detonators mercury fulminate may be found intimately mixed with potassium chlorate. It is, however, used without admixture in certain types of detonators, in the fuzes of high explosive shell and for other military purposes. It is usually purchased under specifications which provide that it shall be at least 98% pure, shall be free from acid, and contain not more than 2% insoluble matter, 1% free mercury, and 0.05% chlorine in the form of chlorides.

Preparation of Sample.—Mercury fulminate being packed and handled in a thoroughly wet condition until dried just before use, it is generally necessary to dry the sample before testing. This may be done by exposing in a low temperature oven at not more than 50° C. until practically dry, then in a desiccator (not a vacuum desiccator) over sulfuric acid or calcium chloride until its weight is constant.

Mercury Fulminate Content.—Exactly 0.3 g. is weighed into a wide-mouthed Erlenmeyer flask of about 250 ml. capacity, and 30 ml. of a 20% solution of purest sodium thiosulfate is added quickly and the mixture shaken for exactly 1 minute. At once titrate with N/10 hydrochloric acid using 3 drops of methyl red indicator, the titration to be commenced 1 minute after adding the sodium thiosulfate, and to occupy not more than 1 minute additional time.

The percentage of mercury fulminate is calculated from the volume of standard acid required, after deducting the volume of acid required for a blank determination. Four molecules of HCl are equivalent to 1 mol. of mercury fulminate, or 1 ml. N/10 HCl equals 0.00711565 g. mercury fulminate. The reaction is assumed to be as follows:

$$HgC_2N_2O_2+2Na_2S_2O_3+2H_2O=HgS_4O_6+4NaOH+C_2N_2.$$

Acidity.—A 10-g. sample is extracted with 2 successive 25-ml. portions of boiled distilled water in a Gooch crucible, and 3 drops of methyl orange solution (1 g. per liter) added to the solution. No red tinge of color should be obtained.

Insoluble Matter.—A 2-g. sample is dissolved in 20% $Na_2S_2O_3$ solution, filtered through a tared Gooch crucible and any insoluble washed several times with water and dried to constant weight at 60°–70° C.

Free Mercury.—The residue of insoluble matter obtained as described above is treated with a solution of 3 g. KI and 6 g. $Na_2S_2O_3$ in 50 ml. H_2O by passing the solution through the Gooch crucible. Any organic mercury compounds are thus converted into mercuric iodide, which is soluble in $Na_2S_2O_3$ solution. The metallic mercury remains behind on the filter, and is washed with H_2O, dried 1 hour at 80°–90° C., and weighed.

Chlorides.—A 5-g. sample of fulminate is extracted in a Gooch crucible with 2 successive 25-ml. portions of distilled water at 90°–100° C. Three drops of concentrated HNO_3 and 10 drops of 10% $AgNO_3$ solution are added to the filtrate. If a turbidity results, the AgCl should be determined gravimetrically or a fresh sample extracted and the filtrate titrated with a standard $AgNO_3$ solution.

Lead Azide

Lead azide, PbN_6, is a primary or detonating explosive. Although it has been employed in several European countries for many years as an ingredient of

detonators and primers for both commercial and military purposes, its use in the United States is comparatively recent. Its principal application is as a priming charge in compound detonators, where it is superimposed on a main charge of tetryl, TNT or other high explosive. Normally a crystalline compound, it is extremely sensitive when in large crystals, and hence is prepared for practical use in the microcrystalline state, or in the form of small rounded aggregates. Its natural white color may be slightly darkened by exposure to light. It should be free from acidity. Its lead content may be regarded as an indication of its purity, provided no other lead compounds are present. Pure PbN_6 contains 71.15% Pb. The sample taken for analysis should be dried at about 95° C.

Acidity.—A 10-gram sample is extracted in a Gooch crucible with 100 ml. of previously boiled, cold distilled water in 20 ml. portions. The filtrate is tested for acidity with methyl orange indicator.

Lead Content.—A weighed sample (approximately 1 g.) is dissolved in 50 ml. of saturated solution of ammonium acetate by warming in a 400-ml. beaker. The solution is diluted with 200 ml. distilled water, heated to boiling, and 10 ml. of a 10% solution of $K_2Cr_2O_7$ added with rapid agitation. After digesting on the steam bath for 1 hour, the precipitate is collected in a Gooch crucible. washed with hot water, dried at 100° C. and weighed. $PbCrO_4 \times 0.64109 = Pb$.

Blasting Caps and Electric Detonators

The commercial blasting caps and electric detonators loaded with a mixture of mercury fulminate and potassium chlorate, which were in general use in the United States up to a few years ago, have now been largely displaced by compound detonators in which a priming charge of mercury fulminate, lead azide, diazodinitrophenol, hexanitromannite or other primary explosive is employed to initiate a main charge of tetryl, TNT, picric acid or other nitrocompound.

Preparation of Sample.—In the examination of blasting caps or detonators for either commercial or military use, the removal of the detonating composition from the copper, aluminum or brass shell requires considerable precaution. Blasting caps are emptied by squeezing the cap gently in a pair of "gas forceps," the jaws of the forceps being passed through a small opening in a piece of heavy leather, rubber belting, or similar material, about 6″ square, which serves as a shield to protect the hand in case of the possible explosion of the cap in squeezing. After each squeeze, the loosened portion of the charge is shaken out on a piece of glazed paper, the cap turned slightly in the forceps and again squeezed. The pressure on the cap should be just sufficient to slightly dent it, and in shaking out the charge, the cap should not be tapped on the table or other surface. With these precautions there is little danger of an explosion. Another method of removing the charge is rolling the cap between two pieces of hardwood board, emptying the loosened portion of the charge after each rolling.

Electric detonators [15] are opened by first cutting off the wires or "legs" close to the shell, then tearing off the upper portion of the shell by means of pointed side-cutting pliers, the cap being held firmly in the fingers and a thin

[15] A safe apparatus for cutting open electric detonators is shown in Bureau of Mines Technical Paper No. 282, "Analysis of Detonating and Priming Mixtures," by C. A. Taylor and W. R. Rinkenbach, Plate I.

strip of the copper shell being torn off spirally by nipping the top edge of the shell with the forceps. This must be done with great care, especially as the portion of the shell containing the fulminate charge is approached. When the greater portion of the plug which holds the wires in place has been exposed, the plug and wires are gently pulled out, care being taken to avoid force and possible friction, and any adhering particles of the charge brushed off onto glazed paper. The charge is then removed from the lower part of the shell just as in the case of blasting caps.

The charge is removed separately from several of the caps or detonators and each weighed in order to determine the average weight of charge as well as variation of same.

" Reinforced " caps, or those which contain a small perforated inner copper capsule pressed on top of the charge, must be opened in the manner described for electric detonators, in order to remove the inner capsule. Detonators of this type usually contain a main charge of some nitro compound superimposed by a layer of mercury fulminate, mixture of fulminate and chlorate, or lead azide. Although a clean mechanical separation of the two layers is usually not possible, portions can be taken from each and identified by qualitative tests before proceeding with a quantitative examination.

Moisture.—The moisture content of the composition is determined by desiccating to constant weight over sulfuric acid or calcium chloride.

Analysis of Composition Containing Mercury Fulminate and Potassium Chlorate.—About 2–3 grams of the well-mixed composition is weighed in a Gooch crucible provided with asbestos mat or disc of filter paper or silk, and first moistened with a few drops of alcohol, then extracted with 200–250 ml. of cold water in 15–20 ml. portions, using slight suction after each portion has remained in the crucible for a few minutes. The residue in the filter is dried to constant weight at 60°–70° C. (2–3 hours), and weighed.

The water extract contains the potassium chlorate and a portion of the mercury fulminate, which is slightly soluble in cold water. It is treated with 2 ml. of ammonium hydroxide and H_2S passed to completely precipitate the dissolved mercury fulminate as HgS. This black precipitate is filtered off, washed, dried and weighed. Its weight $\times 1.22$ gives the amount of mercury fulminate dissolved by the water. This weight added to the weight of the dried residue insoluble in water gives the total weight of mercury fulminate in the sample. The $KClO_3$ is found by subtracting the per cent of mercury fulminate + per cent moisture from 100%.

Analysis of Compositions Containing Nitrocompounds.—Trinitrotoluene, tetryl or picric acid can be identified by melting point test, TNT melting at about 79°–80° C., tetryl at about 128° C., and picric acid at about 120°–122° C. They may be extracted from the mixture by means of ethyl ether, in which mercury fulminate is only very slightly soluble, and the determination of $KClO_3$ and mercury fulminate then made as described in the preceding paragraph.

If the main charge is an organic nitrate such as nitrated vegetable ivory, nitrostarch, nitromannite etc., such material will be left with the mercury fulminate in the insoluble residue after extraction with water. The mercury fulminate is then extracted by means of a hot 20% solution of sodium thiosulfate, leaving the organic nitrate in the Gooch crucible. These materials in the detonating composition can be readily identified by microscopic examination.

In detonators where TNT or tetryl compose the main portion of the charge, a small amount of lead azide, with or without mercury fulminate, may be used as a priming charge for the purpose of initiating the detonation of the nitrocompound. It should be identified in the top portion of the charge, next to the reinforcing cap, and will in all probability be present if mercury fulminate is not found. It is practically insoluble in water and in ether, and will be left in the insoluble residue. If present, fulminate is destroyed by treating the residue, in a flask, with 25 ml. of KOH solution. This converts the lead azide to potassium azide, KN_3. A slight excess of H_2SO_4 is added and the mixture distilled, the distillate, containing HN_3, being collected in water. Enough NaOH is added to the distillate to give an alkaline reaction with litmus, then a little $Pb(NO_3)_2$, when lead azide, PbN_6 will be regenerated as a white precipitate, which may be filtered off, washed with water, then with alcohol, dried in the air, and tested by striking a small portion with a hammer.

Primers

Variations in Composition.—Many varieties of composition are used in primers for small arms ammunition, and for other military purposes. The composition must be ignited by the impact of the firing pin, and must give a flame of sufficient intensity and duration to ensure proper ignition of the propellant or of the detonator, depending on the purpose for which the primer is employed. As primers are used with various kinds and granulation of explosives, a priming composition suitable for one purpose is unsuited for another; hence there are many types of priming compositions. A few of the types which were in common use up to comparatively recent years are shown in Table 1 below. Table 2 gives a few examples of the great variety of patented types of the more modern " non-corrosive " primer compositions, in which potassium chlorate is eliminated because the chloride formed as one of the products of combustion was found to be responsible for corrosion of the gun barrels. " Non-corrosive " primers have displaced many of the older types.

TYPES OF PRIMER COMPOSITIONS
APPROXIMATE COMPOSITION (PER CENT)

Table 1

Ingredients	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
Mercury fulminate	31	25	11	—	—	—	—	—	—	28
Potassium chlorate	38	38	53	60	50	51	53	53	47	14
Sulfur	—	—	—	7	3	9	—	—	22	—
Powdered glass	—	—	—	—	—	12	—	—	—	35
Lead sulfocyanate	—	—	—	—	—	—	25	25	—	—
Copper sulfocyanate	—	—	—	3	—	—	—	—	—	—
Barium nitrate	—	6	—	—	—	—	—	—	—	—
TNT	—	—	—	—	—	—	5	—	—	—
Tetryl	—	—	—	—	—	—	—	3	—	—
Antimony sulfide	31	31	36	30	44	26	17	17	31	21
Lead oxide (PbO)	—	—	—	—	—	—	—	2	—	—
Shellac	—	—	—	—	—	2	—	—	—	2
Black powder (meal)	—	—	—	—	3	—	—	—	—	—

TABLE 2

Mercury fulminate	—	30–35	25–40	—	30–31.5	37	35–40
Lead styphnate	38	—	5–10	—	10–5.5	—	—
Barium nitrate	39	—	24–44	—	29–30.5	32	0–16
Lead nitrate	—	—	—	30	—	—	30–12
Lead peroxide	5	—	—	—	—	—	—
Barium peroxide	—	25–45	—	—	—	—	—
Calcium silicide	11	10–25	—	—	—	—	—
Antimony sulfide	5	—	0–16	—	—	28	—
Lead sulfocyanate	—	—	—	7	10–10.5	—	12–10
Diazodinitrophenol	—	—	—	6–8	—	—	—
Tetracene	2	—	—	—	—	—	—
Basic lead picrate	—	—	—	38–36	—	—	—
Lead dinitrosalicylate	—	—	4–10	18	—	—	—
Abrasive	—	0–25	0–30	—	20–21	3	22–21

In addition to these ingredients most priming compositions are mixed with small amounts of some binding material dissolved in water or alcohol, such as gum arabic, gum tragacanth, glue, shellac, etc. These traces of binding materials are usually disregarded in the analysis of the compositions.

Preparation of Sample.—If the caps contain anvils, these must first be carefully removed, as well as any covering of tin foil or paper. The primer composition is then carefully removed from a number of primers and weighed to determine the average charge. It is then carefully crushed, a little at a time, and the sample well mixed. If necessary, it may be removed from the caps by the aid of water or alcohol and the latter removed by evaporation before weighing.

Qualitative Examination.—The following special tests may be made use of in connection with a qualitative analysis of the mixture:

A small amount is burned between two watch glasses, the formation of a mirror indicating mercury, antimony, copper or lead. The mercury mirror is readily volatile on gentle ignition.

Extract a portion of the mixture with ether, then with water, then with $Na_2S_2O_3$ solution, then with aqua regia, retaining each of these solutions.

TNT or tetryl may be present in the ether solution and are identified by m.p. or color test, TNT giving a deep red color with acetone and KOH. Sulfur is detected by burning a portion of the ether-soluble material and noting odor of SO_2.

The water extract is tested for $KClO_3$ by adding H_2SO_4, boiling, and noting odor of chlorine. A portion is treated with HCl and $FeCl_3$, a red color indicating thiocyanate. The usual $FeSO_4$ ring test is made for nitrates. A white precipitate with H_2SO_4 indicates Ba or Pb.

The aqua regia solution is diluted and tested with H_2S for antimony, lead, and copper. If the precipitate is not orange-red, lead or copper are indicated. Dissolve in HNO_3, neutralize with NH_4OH; a blue solution indicates copper, while lead is detected by the formation of a white precipitate with H_2SO_4.

Any material insoluble in aqua regia may be powdered glass or other abrasive material.

Quantitative Analysis.—The method of analysis will depend entirely upon the ingredients indicated by qualitative tests. In general, a separation is best

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effected by successive extractions with ether, water, $Na_2S_2O_3$ solution (to remove fulminate), dilute or concentrated HCl, and aqua regia. The small amount of mercury fulminate present in the water extract may be determined by precipitation with H_2S or by adding 10–15 ml. of thiosulfate solution and a few drops of methyl orange and titrating with N/10 HCl or H_2SO_4 (see page 513 of Vol. I). Other materials in the water and acid solutions are determined by the usual analytical methods.

Nitrocellulose

General.—The term nitrocellulose, or more correctly cellulose nitrate, applies to any nitration product of cellulose, ranging from products containing in the neighborhood of 10–11% N, which are used in the preparation of lacquers and other commercial products, to military guncotton with over 13% N. All of these products are undoubtedly mixtures of the various nitrates of cellulose, as indicated by the fact that there is always some material with low nitrogen content, soluble in ether-alcohol, in high nitrogen guncotton, and some insoluble material in the lower nitrated commercial products. It can usually be shown without great difficulty that any nitrated cotton is a mixture of various nitrates of cellulose.

The products of military importance are the insoluble guncotton of high N-content, and the so-called " pyro " or pyrocellulose, soluble in ether-alcohol and of about 12.60% N-content. In testing these products, the characteristics of most importance are content of nitrogen, solubility in ether-alcohol, and stability. Other determinations generally made are solubility in acetone and ash.

Preparation of Sample.—If the sample contains a large excess of water, it is enclosed in a clean cloth and the excess water removed by means of a press or wringer. The pressed sample is then rubbed up in the cloth (not with the bare hand) until lumps are removed, then spread on clean paper trays in an air bath at about 35°–40° C. until " air-dry."

Samples for stability tests and nitrogen determination are treated as noted below, the air-dry sample being suitable for determining solubility and ash.

Nitrogen.—About 1 to 1.05 g. of the air-dry sample is roughly weighed in a tared weighing bottle, dried at 98°–102° C. for 1½ hours, cooled in a desiccator and accurately weighed. It is then transferred to the generating bulb of a nitrometer (Du Pont modification; see p. 650) using a total of 20 ml. of 94–95% c.p. H_2SO_4. The sample must be dissolved in the acid either in the weighing bottle or in the cup of the generator, before it is drawn into the generating bulb, and both the weighing bottle and the cup of the generator must be thoroughly washed out with the 20 ml. of H_2SO_4, so that none of the sample is lost. The determination in the nitrometer is completed in the usual manner (p. 650), the result being expressed as per cent N in the dried sample of nitrocellulose.

Solubility in Ether-Alcohol.—(*a*) *Guncotton*: The amount of ether-alcohol soluble material in guncotton being usually not more than 10–12%, the determination may be made by evaporating a clear solution. Two grams of air-dry sample is placed in a clean dry cork-stoppered 250-ml. cylinder, 67 ml. of 95% ethyl alcohol added to thoroughly wet the guncotton, then 133 ml. of

ethyl ether (U.S.P. grade, 96%), added and the mixture well shaken. If the mixture of 2 parts ether and 1 part alcohol be added at once to the sample, a gummy mass may result which dissolves with great difficulty, especially if the solubility is unusually high.

The cylinder is now allowed to stand at a constant temperature of usually 15.5° C. The solubility of nitrocellulose *increases* as the temperature is *decreased*, hence a constant temperature of digestion is important. During the digestion, which requires at least 1 hour, the cylinder must be thoroughly shaken at 5-minute intervals. The cylinder is now allowed to stand for at least 4 hours, until the insoluble portion of the sample has completely settled and the supernatant liquid is perfectly clear.

Fifty ml. of the clear solution is now drawn off with a pipette, care being taken not to disturb the settled pulp, and evaporated in a weighed evaporating dish on a steam bath, avoiding loss from violent boiling of the ether. When 25–30% of the solution has been evaporated, 10 ml. of distilled water is added slowly and the evaporation continued to dryness. The effect of the water is to leave the residue in a white, brittle or powdery condition, rather than a tough film which would lose its solvent with difficulty.

The dish is finally placed in an oven at 95–100° C. for ½ hour, cooled in a desiccator, and weighed. The weight of the residue, corrected for the residue in the 50 ml. of ether-alcohol and 10 ml. H_2O used, represents the soluble nitrocellulose in 0.5 g. of the guncotton.

(*b*) *Pyrocellulose:* The solubility of pyrocellulose may be determined in the manner described for guncotton, but owing to the much larger amount of soluble material present, the evaporation of the residue to constant weight without decomposition involves considerable difficulty. Sufficient water must be added to precipitate the soluble nitrocellulose from solution in a stringy or fibrous condition.

The determination is usually conducted by either the volumetric method or the gravimetric method.

In the volumetric method, one gram of the air-dry sample is covered with 75 ml. of 95% ethyl alcohol and allowed to stand for about 2 hours with frequent stirring, 150 ml. of ethyl ether is then added with stirring and the agitation continued until solution is complete. The solution is now allowed to stand at least 4 hours with frequent stirring, during at least 1 hour of which time it is to be kept at a temperature of 15.5° C. It is then transferred to a " solubility tube " and allowed to stand for about 16 hours, in order that the insoluble material may settle completely. The solubility tubes are heavy glass tubes about 21 inches long and 1.35 inches inside diameter, tapering gradually near the bottom to a constricted portion about 2 inches long and about 0.3 inch inside diameter. This narrow bottom portion is graduated in one-tenth ml. The volume of the settled insoluble material is read in ml. from the scale on the tube. If the reading is 0.25 ml. or less, the percentage of insoluble is considered to be 1% or less. If an exact determination is desired the gravimetric method must be used.

In the gravimetric method the solution is prepared and settled in a solubility tube as described above and the clear liquid removed as completely as possible by means of a narrow siphon tube of glass. Fresh alcohol and ether are then added as before, the tube shaken and allowed to stand again until the

insoluble has settled, when the process may be repeated several times, depending on the amount of insoluble material present. After the last decantation, the residue is washed from the tube to a beaker, using as small a quantity of ether-alcohol as possible, and the mixture filtered through a weighed Gooch crucible with ignited asbestos mat, the insoluble washed free from soluble nitrocellulose with ether-alcohol, dried first at a low temperature and finally at 100° C. to constant weight, cooled and weighed. The crucible is then carefully ignited over a free flame, cooled and weighed again. The loss of weight on ignition is considered as insoluble nitrocellulose.

Solubility in Acetone.—A 1-gram sample of air-dry pyrocellulose is treated with about 200 ml. of acetone with frequent stirring until all gelatinous matter has dissolved. The solution is transferred to a solubility tube (described above), well shaken and allowed to settle for about 16 hours. If the volumetric reading is 0.2 ml. or less, the percentage of insoluble is considered to be 0.4% or less. A gravimetric determination may be made as described in the preceding paragraph.

Ash.—One gram of air-dry sample is weighed in a tared crucible, moistened with 10–15 drops of concentrated nitric acid, and digested for 2–3 hours on a steam bath until converted to a gummy mass. The crucible is then heated carefully over a Bunsen burner until the mass is completely charred, then at a red heat until its weight is constant. The residue is the ash of the sample.

Stability Test: Heat Test with Potassium Iodide Starch Paper.—The " heat test " or KI test, as it is commonly designated, is the test most commonly employed for determining the stability or degree of purification of nitrocellulose, whether guncotton or pyrocellulose. This test, also referred to as the Abel test, depends on the action of oxides of nitrogen liberated by the nitrocellulose under the influence of heat, the gases in contact with the KI-starch paper liberating iodine which colors the starch.

The sample is dried with great care to avoid contamination, in a clean paper tray, at 35° to 40° C., until its moisture is reduced to the amount which will give the minimum heat test, usually 1.5 to 2%. The proper amount of moisture is determined as follows: During the progress of the drying, the sample on the tray is " rubbed up " from time to time, using a piece of clean tissue paper spread over the back of the hand. When the sample begins to adhere to the paper, due to static electricity, a sample of 1.3 g. is weighed into a standard test tube. These tubes are 5½ inches long, not less than ½ inch inside diameter and not more than ⅝″ outside diameter, made of glass about 3/64 inch (1.2 mm.) thick. As soon as the first sample is weighed, the tray is replaced in the drying oven for 2–5 minutes, a second sample weighed, and this process repeated until a series of 5 samples have been taken, the last sample being completely dry. This series of samples, if properly taken, will cover the range of moisture content giving the minimum heat test. If the sample in the tray appears to have become too dry during the time the weighings are being made, it may be placed in a moist atmosphere for not more than 2 hours; the entire time of drying and making the test must not exceed 8 hours.

The tubes containing the samples are fitted with clean, fresh cork stoppers through which pass a piece of glass rod into the end of which is fused a small piece of platinum wire bent into a hook. The wire is heated in a flame to clean it, a piece of the standard KI starch test paper, 1″×⅜″, attached, taking care

that neither wire nor paper are touched with the fingers, and the paper moistened on its upper portion by touching it with a glass rod dipped in a solution of equal volumes of pure glycerin and water. The stoppers are then inserted in the tubes and the tubes placed in a constant temperature water bath, so that they are immersed to a depth of 2.25 inches. The time of placing in the bath and the time of the appearance of the first faint yellowish discoloration of the test paper are noted. The minimum test given by the 5 samples is taken as the result of the test. The discoloration appears at the lower edge of the moist portion of the paper. The temperature of the heat test bath is 65.5° C. (150° F.) for pyrocellulose, and usually 76.5° C. (170° F.) for guncotton. Pyro is usually required to stand a test of 35 minutes, and guncotton 10 minutes.

A standard test paper is absolutely essential, and is prepared as follows: [16]

The paper used in preparing the test paper is Schleicher and Schüll's filter paper 597. This is cut in strips about 6 by 24 inches, and after being washed by immersing each strip in distilled water for a short time is hung up to dry overnight. The cords on which the paper is hung are clean and the room is free from fumes. The washed and dried paper is dipped in a solution prepared as follows:

The best quality of potassium iodide obtainable is recrystallized three times from hot absolute alcohol, dried, and 1 gram dissolved in 8 ounces of distilled water. Cornstarch is well washed by decantation with distilled water, dried at a low temperature, 3 grams rubbed into a paste with a little cold water, and poured into 8 ounces of boiling water in a flask. After being boiled gently for 10 minutes, the starch solution is cooled and mixed with the potassium iodide solution in a glass trough.

Each strip of filter paper is immersed in the above-mentioned mixture for about 10 seconds and is then hung over a clean cord to dry. The dipping is done in a dim light and the paper left overnight to dry in a perfectly dark room. Every precaution is taken to insure freedom from contamination in preparing the materials and from laboratory fumes that might cause decomposition. When dry the paper is cut into pieces about ⅜ by 1 inch and is preserved in the dark in tight glass-stoppered bottles, the edges of the large strips being first trimmed off about one fourth inch to remove portions that are sometimes slightly discolored. When properly prepared the finished paper is perfectly white, any discoloration indicating decomposition due to contamination.

Stability Test at 134.5° C.—In addition to the KI starch test, pyrocellulose is usually required to stand a test at 134.5° C., made as follows:

The sample is completely dried at about 40° C., and 2.5 grams placed in each of 2 heavy glass tubes, 290 mm. long, 18 mm. outside diameter and 15 mm. inside diameter, closed with a cork stopper through which passes a hole 4 mm. in diameter. A strip of litmus paper or standard normal methyl violet paper, 70 mm. long and 20 mm. wide, is placed in each tube, its lower edge 25 mm. above the sample, which is pressed down to occupy a depth of 2 inches, the walls of the tube being wiped clean with a roll of paper. The tubes are then heated in a constant temperature bath at 134° to 135° C., all but about 6–7 mm. of the tube being immersed in the bath. They are partially withdrawn for

[16] Storm, C. G., Proc. 7th Inter. Congress Appl. Chem., 1909; J. Ind. Eng. Chem., **1**, 802 (1909).

examination of the test papers every 5 minutes after the first 20 minutes of heating, and replaced at once. The time required for reddening of the litmus paper or for turning the methyl violet paper to a salmon pink color is noted as the time of the test. A minimum test of 30 minutes is required with the methyl violet paper, and heating is then continued for a total of 5 hours, during which time there should be no explosion.

The standard normal methyl violet paper is prepared as follows:

Preparation of Methyl Violet Test Paper.—A solution is prepared containing the following ingredients: pure rosaniline acetate prepared from 0.2500 g. pararosaniline, .1680 g. methyl violet (crystal violet), 6 ml. c.p. glycerin, 30 ml. water, and sufficient pure 95% ethyl alcohol to make up to 100 ml. This solution is placed in the angle of an inclined deep rectangular glass tray, and large sheets of Schleicher & Schüll filter paper (No. 597) cut in four strips are dipped in it. In dipping, the strip is held by one end and dipped to within ¼″ of this end, withdrawing it slowly up the side of the tray so as to remove surplus solution. The strip is then held horizontally and waved to and fro so as to prevent the solution from running and collecting in spots. As soon as the alcohol has evaporated the strip is suspended vertically to dry, and when dry is cut in strips 20×70 mm. These strips are bottled and kept for use in the 134.5° C. test.

Viscosity.—In the case of commercial nitrocelluloses it is frequently necessary to determine the viscosity of standard solutions. The solutions used for this purpose are usually as follows:[17]

Formula	% by Weight		
	A	*B*	*C*
Nitrocellulose (dried at 50° C.)	12.2	20.0	25.0
Ethyl acetate (85–88% grade)	17.5	16.0	15.0
Denatured alcohol, C.D. No. 5 (188–190 proof)	22.0	20.0	18.75
Toluol (2° C. range, incl. 110.7°)	48.3	44.0	41.25

Formula *A* is used unless viscosities obtained with it are 6 seconds or less, in which case Formula *B* is used. If *B* gives below 3 seconds Formula *C* is used.

A glass cylinder 1″±0.02″ inside diameter and 14″ high, with marks 10″ apart at points 2″ and 12″ from the top, is filled with the solution to be tested, the cylinder stoppered and allowed to stand until all bubbles have disappeared, then brought to a temperature of 25°±0.1° C. A steel ball 0.312″ to 0.313″ in diameter, weighing 2.035 g.±0.01 g., is then released at the center of the surface of the solution, and the number of seconds required for the ball to pass through the 10-inch column of solution between the marks on the cylinder is recorded as the viscosity of the sample with the Formula used.

[17] A. S. T. M. Standard Specification for Soluble Nitrocellulose (D 301–331).

SMOKELESS POWDER

Nitrocellulose Powders

At the present time the smokeless powder used by all nations is composed of either colloided nitrocellulose or a mixture of colloided nitrocellulose and nitroglycerin with or without the addition of other ingredients. All cannon powder used in this country is of the nitrocellulose type, small-arms powders being of both types. The form and size of the grains are of great variety, depending on the arm in which the propellant is to be employed.

Physical tests made in connection with the examination of smokeless powder include the compression test, determinations of average measurements of the grains, specific gravity, gravimetric density, number of grains per pound, and calculation of burning surface per pound.

Chemical tests include determinations of moisture and volatile solvent, diphenylamine used as stabilizer, ash, material insoluble in ether-alcohol and in acetone, and sometimes nitrogen content.

Stability tests include the 134.5° C. test, and the "Surveillance test."

Moisture and Volatiles.—A sample of the powder weighing approximately 1 gram, in the form of thin shavings cut from at least 10 grains, or of whole grains if the powder is too small to cut conveniently, is placed in a clean, dried and weighed 250-ml. beaker, 50 ml. of 95% (by volume) alcohol, and 100 ml. ethyl ether added and the beaker allowed to stand under a cover-jar with occasional stirring, until the powder is completely dissolved. This usually requires from 1 to 2 days. When all gelatinous particles of the powder have dissolved, the beaker is heated on the steam bath to evaporate a part of the ether, before precipitation of the nitrocellulose with water. The amount of ether to be evaporated is important, since it largely determines the character of the nitrocellulose precipitate. The presence of too much ether causes a fine sandy precipitate; too little causes a gummy, gelatinous precipitate. A fine, flaky, or fibrous precipitate is desirable. The proper amount of evaporation can be best determined by practice; usually the solution may be evaporated to about 2/3 its original volume before precipitating. When the proper volume is obtained, 50 ml. of water is added from a graduate, with continual stirring, in 5 ml. portions. If a thick gummy precipitate forms, add a little ether until it becomes flaky; then add the remainder of the 50 ml. of water. The heating is continued with stirring, until most of the ether has evaporated, and the beaker is then left on the bath until the precipitate is just dry. It is then placed in the 100° C. oven for 1 hour, cooled in a desiccator, and weighed as rapidly as possible. To facilitate weighing the weights should be placed on the balance pan before the beaker is removed from the desiccator, so that the exact weight can be adjusted quickly. If more than 10 seconds are consumed in this weighing, the error caused by absorption of moisture from the air is an appreciable one. In any event a check weighing should be made after an additional 30 minutes drying at 100° C.

Absorption of moisture during weighing may be avoided by the use of a suitable aluminum beaker provided with a tightly fitting cover, instead of an ordinary glass beaker.

The final weight of nitrocellulose precipitate subtracted from the weight of the original sample represents the weight of moisture and volatile solvent, and is calculated as per cent of the original sample. If the powder contains diphenylamine, this result is corrected by subtracting from it one fourth of the total diphenylamine content, it having been ascertained by actual trial that approximately this proportion of the diphenylamine is volatilized during the evaporation.

If the powder contains other organic constituents which would be more or less completely volatilized during the evaporation process described above, resort must be had to an indirect method of determining the content of volatile solvent. In such a case, the diphenylamine and other ether-soluble constituents are removed by long continued ether extraction of the finely sliced or crushed grains of powder, the ether extract is evaporated almost to dryness in a slow current of dry air and finally brought to constant weight in a sulfuric acid desiccator. The volatile solvent is taken as the difference between 100% and the sum of the percentages of ether extract, nitrocellulose and moisture.

Moisture.—An approximation to the actual moisture content of the powder can be obtained by drying a sample of not less than 2 whole grains and not less than 20 grams for 6 hours in a vacuum oven having a vacuum of not less than 25 inches and maintained at 55±2° C., cooling in a desiccator and weighing, the loss of weight being regarded as equal to the hygroscopic moisture in the powder.

Diphenylamine.—The content of diphenylamine used as a stabilizer in smokeless powder is most conveniently and rapidly determined by the " nitration method " as follows:

Five grams of the powder in small grains or slices is treated with 30 ml. of concentrated HNO_3 in a 250-ml. beaker, covered with a watch glass and heated on the steam bath until the powder has been completely decomposed. The solution is then cooled and added to 100 ml. of cold distilled H_2O in a second beaker, stirring vigorously, the first beaker being washed out completely into the second, using additional water. This mixture is now heated on the steam bath until the flocculent precipitate has settled and the liquid has a clear yellow color. It is then cooled, filtered through a weighed Gooch crucible, the precipitate dried at 100° C. and weighed. The weighed precipitate is now dissolved by extracting with acetone, the crucible dried and weighed again, the loss of weight being the nitrodiphenylamine produced by action of the HNO_3 on the diphenylamine. This nitrodiphenylamine is a mixture of nitroproducts, and the empirical factor 0.4345 has been determined for converting it to its equivalent in diphenylamine.

It is obvious that the diphenylamine found in old powders by the above method will include any of the original diphenylamine which has been acted on by nitric acid resulting from slow decomposition of the nitrocellulose and thereby converted to nitro derivatives of diphenylamine. The nitration method therefore determines " Total diphenylamine." The content of free or " active " diphenylamine is determined by the bromination method as follows:[17a]

The ether extract, obtained as described in the paragraph on Moisture and Volatiles, is dissolved in about 100 ml. of ether, transferred to a 250-ml. beaker, and 0.2 ml. bromine added. The solution is heated to about 75° on a steam bath and the ether evaporated with a current of dry air. The residue is treated

[17a] S. G. Cook, Ind. Eng. Chem. Anal. Ed., 7, 250 (1935).

with 40 ml. of 95% (by volume) ethyl alcohol, heated to boiling, 40 ml. of hot water added and the beaker left on the steam bath for exactly 10 minutes. The precipitate of tetrabromidiphenylamine is collected by filtering the hot liquid through a Gooch crucible, washed with 80 ml. of boiling 47.5% (by volume) ethyl alcohol, and finally with hot water, dried 1 hour at 100° C. and weighed. The weight of precipitate multiplied by 0.3487 equals weight of diphenylamine.

Ash.—The ash is determined in the manner described for nitrocellulose (p. 1692), the sample being in the form of slices or small grains, and the digestion with HNO_3 continued until decomposition is practically complete, before heating over a flame.

Solubility in Ether-alcohol.—One gram of the sample in slices or small grains is dissolved in 150 ml. of ether-alcohol (2 : 1) in the same manner as for the determination of moisture and volatiles, and transferred to a standard solubility tube (p. 1691), washing it in completely with fresh ether-alcohol so as to bring the total volume to 300 ml. The insoluble material is determined as in pyrocellulose (p. 1691).

Solubility in Acetone.—This determination is made in the same manner as the solubility in ether-alcohol, described above.

Stability Test at 134.5° C.—This test is made on duplicate samples in the same manner as described for pyrocellulose (p. 1693). The samples weigh 2.5 grams and are in as nearly whole grains as is consistent with this weight of sample, large grains being split longitudinally so as to fit the standard tubes. The samples are required to stand heating at 134°–135° C. for 5 hours without explosion and must not turn the normal methyl violet paper to salmon pink color in less than one hour.

" Surveillance Test " at 65.5° C.—Three samples of approximately 45 grams of powder in whole grains, or, in the case of very large grains, 5 whole grains, are placed in 8-ounce wide-mouth glass stoppered bottles, the stoppers having been previously ground so as to fit tightly. These bottles are then heated in a constant temperature magazine at 65.5°±2° C. They are observed several times daily and the time noted when visible fumes of oxides of nitrogen appear in any bottle. The number of days which powder will stand this test depends on the web thickness of the grain, as well as on actual stability and may amount to several hundred days. The test is therefore not a laboratory test, but one which more nearly approaches service conditions. It is of great value as an indication of the possible " stability life " of the powder in service.

Nitrogen.—The determination of nitrogen in smokeless powder is not usually necessary, in as much as the powder is usually made from nitrocellulose of known nitrogen content, but when desired the determination is made as follows, in the case of powders containing only colloided nitrocellulose and diphenylamine.

An average sample of about 5 grams of the powder in slices or small grains is dissolved in acetone (100 ml. to each 1 g. of sample). When the sample is dissolved, the solution is added drop by drop, preferably from a burette, to 200 ml. of hot water in a beaker, the beaker being immersed in boiling water so as to maintain its contents at about 90° C. During this addition the hot water is continually stirred with a glass rod, so that the precipitated nitrocellulose forms stringy masses which wrap about the rod. Small accumulations

of the precipitate are transferred frequently from the rod to another beaker of hot water to prevent the formation of a colloided mass. When 2 g. or more of the precipitate has been collected and the acetone has been volatilized by the hot water, it is removed from the beaker and dried at 35°–40° C. About 1 g. of this dry precipitate is placed in a tared weighing bottle, dried 1 hour at 100° C., weighed, and transferred to the cup of the nitrometer with sulfuric acid. Part of the acid should be added to the precipitate in the weighing bottle before transferring to the nitrometer in order to avoid loss of the dry precipitate in handling. The determination of N is then completed as in the case of nitrocellulose (page 1690). If the powder contains diphenylamine, a correction is necessary for the amount of diphenylamine retained by the precipitated nitrocellulose. This has been found to be an added correction of 0.15% N in the case of powders containing the usual amount of 0.4% diphenylamine. This correction compensates for the nitrogen which becomes combined with the diphenylamine, converting it to nitrodiphenylamines.

Instead of correcting for the effect of the diphenylamine, the latter may be removed from the precipitated nitrocellulose, after air-drying and before final drying at 100° C., by extraction with pure anhydrous ether. Results are quite accurate if the determination is conducted with proper precaution.

Muraour [18] describes the following method for direct determination of nitrate nitrogen in smokeless powders without preliminary treatment: The powder sample is dissolved in acetone and the solution treated with hydrogen peroxide and sodium hydroxide with gentle warming. Sodium perborate is then added and the mixture reduced with Devarda alloy in the presence of additional sodium hydroxide, and finally distilled into a known volume of standard sulfuric acid. Results are obtained which agree closely with the theory. The method is applicable in the presence of easily nitrated materials such as diphenylamine, Centralite, etc., which interfere with the determination of nitrate nitrogen by means of the nitrometer.

Nitroglycerin Smokeless Powders

Powders of this type are composed mainly of nitrocellulose and nitroglycerin and may contain other organic or inorganic substances, such as vaseline, nitro-substitution compounds, substituted ureas or other flame-reducing or surface-coating agents, diphenylamine, metallic nitrates, carbonates, etc. The nitrocellulose may be either high-nitration guncotton insoluble in ether-alcohol, as in British cordite, or a low-nitration product soluble in nitroglycerin, as in ballistite, or may be a mixture of the two varieties.

The method of analysis usually employed consists of (1) an extraction of the nitroglycerin, nitrosubstitution compounds, vaseline, and other ether-soluble materials by means of anhydrous ether; (2) an extraction of the water-soluble materials; (3) determination of soluble and insoluble nitrocelluloses by separation with ether-alcohol (2 : 1).

The extraction with ether is usually made in a Soxhlet apparatus, using about 20 grams of the powder in slices or small grains, in a paper extraction thimble. About 4 hours is usually required for complete extraction. The

[18] Direct determination of nitrate nitrogen in colloided smokeless powders, Henri Muraour, Bull. Soc. Chim. de France (4), **45**, 1189 (1929).

ether extract is evaporated to dryness in a tared glass dish under a bell-jar evaporator (page 1664), and the ether-soluble residue weighed. To determine whether it contains other substances than nitroglycerin, it may be poured in small portions at a time into about 20 ml. of concentrated nitric acid (40° Be) heated on a steam bath. The oxidizing action of the nitric acid destroys the nitroglycerin, and the mixture is then poured into 50–100 ml. of water. Any vaseline or similar substances separate, together with any nitrosubstitution compounds in their original condition or more completely nitrated, diphenylamine in the form of a nitroderivative, etc.

These materials may be separated with more or less completeness by fractional crystallization from ether or other solvent. The exact method to be followed depends on the nature of the materials present.

The residue insoluble in ether is dried and weighed, and then transferred to an Erlenmeyer flask and digested in warm water until any water-soluble materials present have been dissolved. The mixture is filtered, the residue washed with hot water, dried and weighed. The filtrate containing the water-soluble ingredients is examined by the usual analytical methods for inorganic ingredients.

The nitrocellulose insoluble in water is tested for nitrogen content, solubility in ether-alcohol and solubility in acetone, by the methods already described.

The dialkyldiphenyl ureas, known as Centralites, are used as surface coating agents and stabilizers in some powders containing nitroglycerin and nitrocellulose. In the analysis of such powders both the nitroglycerin and Centralite are dissolved by extraction with absolute ether, and a mixture of these ingredients obtained by evaporation of the ether. Determination of the nitroglycerin in this mixture by means of the nitrometer gives low results because when concentrated sulfuric acid is added the Centralite becomes nitrated to a tetranitrocompound. Levenson [19] has found that the Centralite in such mixtures can be determined directly by a bromination method, as follows:

Extract 5 grams of the finely ground powder with absolute ether for about 24 hours, and evaporate the ether extract to constant weight. Transfer the liquid residue to a 250-ml. glass-stoppered Erlenmeyer flask with 50 ml. of ethyl alcohol, add 25 ml. of standard bromate-bromide solution, cool to 20° and add 5 ml. of concentrated HCl. Stopper the flask, shake gently, and exactly 30 seconds from the time of addition of the acid add 10 ml. of a 15% solution of KI. Immediately titrate the liberated iodine with 0.1 N $Na_2S_2O_3$ solution using starch indicator. 1 ml. 0.1 N $Na_2S_2O_3$ equals 0.0067044 gram diethyldiphenylurea. The nitroglycerin is calculated by difference. To prepare the bromate-bromide solution dissolve 5.568 g. $KBrO_3$ and 30 g. KBr in water and dilute to 1 liter. Standardize by placing 25 ml. of the solution and 50 ml. of ethyl alcohol in a 250-ml. glass-stoppered Erlenmeyer flask, cooling to 20°, adding 5 ml. of concentrated HCl, and after 30 seconds titrating as above with 0.1 N thiosulfate solution. The volume of thiosulfate solution required in the standardization minus that required for the sample represents the Br combined with the Centralite.

[19] Determination of Centralite in double-base smokeless powders, H. Levenson, Ind. Eng. Chem., Anal. Ed., 2, 246–247 (1930).

Typical Compositions of Commonly Used Explosives

Black Blasting Powder

Sodium nitrate	73
Charcoal	16
Sulfur	11 (Bur. of Mines, Bull. No. 80, p. 19)

Black Military Powder

Potassium nitrate	75
Charcoal	15
Sulfur	10

Typical Dynamite formulas—40% grades (Bur. Mines, Bull. No. 80, p. 21)

	Nitroglycerin	Nitro-Substitution Com.	Ammonium Nitrate	Sodium Nitrate	Nitrocellulose	Wood Pulp	Calcium Carbonate
40% straight Nitroglycerin Dynamite	40	—	—	44	—	15	1
"40%-strength" Ammonia Dynamite	22	—	20	42	—	15*	1
"40%-strength" Gelatin Dynamite	33	—	—	52	1	13*	1
"40%-strength" Low-freezing Dynamite	30	10	—	44	—	15	1
"40%-strength" Low-freezing Ammonia Dynamite	17	4	20	45	—	13*	1

* Sometimes contains also flour, cornmeal, sulfur, etc.

Granulated Nitroglycerin Powder ("Judson Powder")

Nitroglycerin	5	10
Combustible material†	35	26
Sodium nitrate	60	64

† Composed of sulfur, coal, and rosin.

Coal Mining Powders. (Permissible Type)

	I	II	III	IV	V	VI
Nitroglycerin	25	15	10	—	—	10
TNT	—	5	—	5	—	—
Ammonium nitrate	—	—	79	90	94	70
Sodium nitrate	34	35	—	—	—	—
Sodium chloride	—	—	—	—	—	9
Wood pulp	15	12	10	—	—	10
Flour	25	17	—	5	—	—
Aluminum powder	—	—	—	—	3	—
Charcoal	—	—	—	—	3	—
Calcium carbonate	1	1	—	—	—	1
Zinc oxide	—	—	1	—	—	—
Magnesium sulfate, cryst	—	15	—	—	—	—

FIXED OILS, FATS AND WAXES

PETROLEUM

It will be remembered that the *fixed oils* are those which leave a permanent stain on paper, whereas the essential or volatile oils evaporate. The fixed oils, if saponifiable, are glycerides of the higher fatty acids, oleic, $C_{17}H_{33}COOH$, stearic, $C_{17}H_{35}COOH$, palmitic, $C_{15}H_{31}COOH$; and if unsaponifiable, hydrocarbons usually of the paraffin (C_nH_{2n+2}) and olefin (C_nH_{2n}) series. The *fats* differ from the oils in having a higher melting-point, caused by a larger percentage of stearic and palmitic acid. The *waxes* differ from the oils or fats in that the former are esters of monatomic alcohols. The oils are further divided according to their drying power on exposure to the air, into drying, semi-drying and non-drying oils.

The drying oils contain a large proportion of glycerides of the unsaturated acids, particularly linoleic and linolenic, whereas the semi-drying contain a smaller percentage, and the non-drying little or none of these esters.

Examination of an Unknown Oil

There being no specific tests for the various oils, as for their identification, the analyst should, in attacking an unknown oil, ascertain all possible facts about it, as the source, the use to which it is put, and the cost.

Certain physical properties too, may aid in the examination. The *color* is of little assistance, as oils may be colored by the use of oleates or butyrates of iron or copper. *Fluorescence* or " bloom " is valuable as indicating the presence of mineral oil; this can be shown [1] by placing a few drops of the oil on a sheet of ebonite and observing the bluish color. The *odor* and *taste* are particularly valuable. Marine animal oils are detected, especially when warm, by their strong " fishy " odor, while neatsfoot, tallow, lard, rosin and linseed oils each have a well-marked and easily distinguishable smell. Whale oil is said to have a " nutty," and rape oil has a harsh, unpleasant " turnipy " taste. The *turbidity*, showing the presence of water, or of oils which imperfectly mix—as castor and mineral oils—and the *sediment*, either stearin or dirt, are also to be noted; these should be filtered out through paper before the oil is analyzed.

The **elaidin** test (page 1765) may be applied next, to allow time for the cake to form; it will be followed by the **Maumené** test (page 1766) both being done in duplicate. In making the elaidin test it is advisable to carry on an experiment under the same conditions with a known sample of lard oil. These two tests will show whether the sample under examination is a drying or non-drying oil and when the ingredients of the mixture are determined, the results of the Maumené test can be used for calculating their relative amounts. The **iodine** test can be employed to check this result.

[1] Outerbridge, Chem. Abstr. 5, 3350, uses an enclosed arc light giving ultraviolet light and makes it quantitative.

Chapter contributed by the late Augustus H. Gill.

The **saponification** test, unless mineral or rosin oil be suspected, need rarely be resorted to; the reason being that it would show practically nothing regarding the nature of the oil. Except in the case of castor (Sapn. No. 181), rape (174), sperm (135) and cocoanut (260), this characteristic is about 193.

Finally, where the importance of the case will warrant, the analyst is advised to prepare a mixture of oils using the proper proportions indicated by the various tests, and subject it to the more rapid tests as the specific gravity, viscosity, Maumené and iodine number. In making out the report of analysis it should be borne in mind that, excepting in the case of the special test, the results of *one* test cannot be relied upon to determine the nature of an oil, but the evidence of all the tests here given should be carefully compared and weighed before rendering a final verdict: in consideration of the fact of the wide variation of the characteristics of the oils, it is futile to report the quantities of oil found in a mixture more closely than 1%.

PETROLEUM PRODUCTS

(a) Burning Oils

The tests or determinations to be made are, in the order of their importance, flash, fire, specific gravity, distillation, sulfur, free acid, sulfuric acid, cloud test, mineral salts and water. In some cases the color is determined as it is of commercial importance.

Flash Test or Point.—By flash point we understand the lowest temperature to which an oil must be heated, to give off vapors which when mixed with air produce an explosive mixture. The results of this test will vary according to the quantity of air over the surface of the oil, and whether this be moving or still; also according to the distance of the testing flame from the surface of the oil. Furthermore, the size of this testing flame, the length of its time of action, its form and dimensions, and lastly, the manner of heating the oil, will all influence the result.[2]

Any cause producing the rapid evolution of a large amount of petroleum vapor tends to lower the flash point. Barometric changes are, for practical work, negligible, each 5 mm. causing a variation of but 0.1° C.

Determination by the " New York State Board of Health Tester."—The apparatus, Fig. 238, consists of a copper oil cup, *D*, holding about 10 oz., the quantity usually contained in lamps, heated in a water bath by a small Bunsen flame. The cup is provided with a glass cover, *C*, carrying a thermometer, *B*, and a hole for the insertion of the testing flame—a small gas flame one-quarter of an inch in length.

[2] Engler and Haase, Z. Anal. Chem., **20**, 3, 1881.

Manipulation.—After describing the apparatus minutely, the regulations of the New York State Board of Health say,[3] " (2) The test shall be applied according to the following directions:

" Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup and pour in enough oil to fill it to within one-eighth of an inch of the flange joining the cup and the vapor-chamber above. Care must be taken that the oil does not flow over the flange. Remove all air-bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

" If an alcohol lamp be employed for heating the water bath, the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case exceed three degrees.

" As a flash torch, a small gas jet one-quarter of an inch in length should be employed. When gas is not at hand employ a piece of waxed linen twine. The flame in this case, however, should be small.

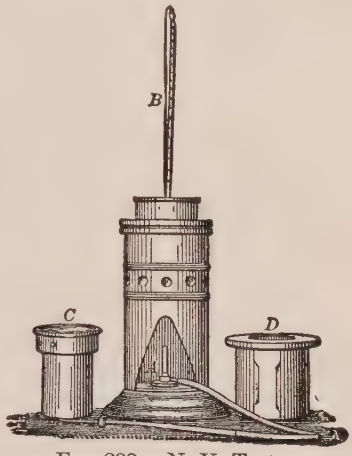


Fig. 238.—N. Y. Tester.

" When the temperature of the oil has reached 85° F. the testings should commence. To this end insert the torch into the opening in the cover, passing it in at such an angle as to well clear the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid and without any pause. This should be repeated at every two degrees' rise of the thermometer until the temperature has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° is reached. After this the lamp may be replaced if necessary and the testings continued for each two degrees.

" The appearance of a slight bluish flame which passes over the entire surface shows that the flashing-point has been reached.

" In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

" The water bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup."

For the determination with the open tester (Tagliabue's small) reference may be had to the author's " Short Handbook of Oil Analysis "; for the test with the closed tester, Abel's or Pensky-Martens, Holde-Mueller, " Examination of Hydrocarbon Oils "; or for the " Tag Tester."

Fire Test.—The fire test of an oil is the lowest temperature at which it will give off vapors which when ignited will burn *continuously*. It is made by continuing to heat the oil (the cover being removed in the case of a closed tester without slipping out the thermometer) at the same rate after the flash test

[3] Report of the New York State Board of Health, 1882, p. 495.

is made and noting the point as indicated above. The flame is extinguished by a piece of asbestos board and the heating discontinued. In the case of many illuminating oils this point is from 10° to 20° F. higher than the flashpoint.

In the case of " Mineral Sperm " (300° F. fire test oil) these tests should be made with the Cleveland open cup. The heating should be at the rate of 10° F. per minute, and the testing flame first applied at 230° F. and then every seven degrees until the flashing-point is reached.

The most satisfactory way of making these tests is to place the watch upon the desk and read the thermometer at the expiration of every minute, noting down each reading in the proper column in the laboratory note-book.

Significance of the Tests.—The flash test rather than the fire test measures the safety of an oil as the vapors producing the flash are evaporated in the fire test. The writer has had samples of oil of 65° to 70° F. flash which gave a fire test of 135°–140° F. These, judged by the flash test are unsafe, whereas they would be passed by the fire test.

Specific Gravity: (*a*) ***By the Hydrometer.***—A hydrometer jar is four-fifths filled with the oil, a verified Baumé hydrometer introduced into it, and the depth read off to which the instrument sinks into the oil. This may be effected by placing a strip of white paper back of the jar and noting the point at which the lower meniscus of the oil touches the scale. The temperature of the oil is taken at the same time, and in case it be not 60° F. (15.5° C.), subtract 1° Baumé from the hydrometer reading, for every 10° F. it is higher than 60°, and add 1° Baumé for every 10° F. it is lower than 60° F. In practice this can be done by Tagliabue's " Manual for Inspectors of Petroleum," which gives the readings at 60° F. for any gravity from 10 to 100° Baumé, between 20° and 109° F. The specific gravity may be found by the formula $\frac{141.5}{131.5+Bé}$, Bé representing the reading Baumé at 15.5° C.

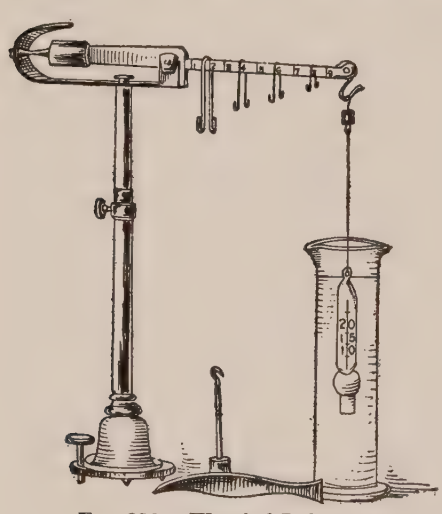


Fig. 239.—Wesphal Balance.

(*b*) ***By the Westphal Balance.***—This is a specially constructed instrument, Fig. 239, with a glass plummet carrying a thermometer counterbalanced by a weight. Upon immersing the plummet in a liquid the positions of the weights, which must be added to restore the equilibrium, represent the specific gravity directly. The largest weight represents the first decimal place, the next the second, and so on. The instrument is placed upon a level table, and by means of the leveling screw is brought into adjustment—i.e., so that the point upon the beam is exactly opposite the point upon the fixed part.

The plummet is now placed in the vial or balance jar containing the oil, cooled to 15.5° C., hung upon the balance, being careful completely to immerse

it in the oil, weights added to restore the equilibrium, and the specific gravity read off as above described.

Care should be taken that the plummet does not touch the sides of the jar or vial. For solid fats and some oils the specific gravity is taken at 100° C., using a special plummet.

Significance of the Test.—The Specific Gravity or "Gravity" as the oil man says shows whether the sample is of paraffine or asphalt base, the latter oils being the heavier.

Distillation Test:

A. S. T. M. Method D 86–35.[4]—Kerosene

STANDARD METHOD OF TEST FOR DISTILLATION OF GASOLINE, NAPHTHA, KEROSENE, AND SIMILAR PETROLEUM PRODUCTS [5]

A. S. T. M. Designation: D 86–35 [6]

Apparatus: ***Flask.***—The standard 100-ml. Engler flask is shown in Fig. 240, the dimensions and allowable tolerances being as follows:

	Centimeters	Inches	Tolerances	
			Centimeters	Inches
Diameter of bulb, outside	6.5	2.56	±0.2	±0.08
Diameter of neck, inside	1.6	0.63	±0.1	±0.04
Length of neck	15.0	5.91	±0.4	±0.16
Length of vapor tube	10.0	3.94	±0.3	±0.12
Diameter of vapor tube, outside	0.6	0.24	±0.05	±0.02
Diameter of vapor tube, inside	0.4	0.16	±0.05	±0.02
Thickness of vapor tube wall	0.1	0.04	±0.05	±0.02

The position of the vapor tube shall be 9 cm.±0.3 cm. (3.55 in.±0.12 in.) above the surface of the liquid when the flask contains its charge of 100 ml. The tube is approximately in the middle of the neck and set at an angle of 75° (tolerance±3°) with the vertical.

Condenser.—The condenser (Fig. 241) consists of a $\frac{9}{16}$-in. (14.29 mm.) OD No. 20 Stubbs Gage seamless brass tube, 22 in. (55.88 cm.) long. It is set at an angle of 75° from the perpendicular and is surrounded with a cooling bath 15 in. long (38.1 cm.), approximately 4 in. (10.16 cm.) wide by 6 in. (15.24 cm.) high. The lower end of the condenser tube is cut off at an acute angle, and

[4] Bureau of Mines Technical Paper 323B is an earlier description.

[5] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[6] This method is issued under the fixed designation D 86; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1921; Adopted in Amended Form, 1927; Revised, 1930, 1935. This method has been approved as American Standard by the American Standards Association.

curved downward for a length of 3 in. (7.62 cm.) and slightly backward so as to insure contact with the wall of the graduate at a point 1 to 1¼ in. (2.54 to 3.18 cm.) below the top of the graduate when it is in position to receive the distillate.

Shield.—The shield (Fig. 241) is made of approximately No. 22 gage sheet metal and is 19 in. (48.26 cm.) high, 11 in. (27.94 cm.) long and 8 in. (20.32 cm.) wide, with a door on one narrow side, with two openings, 1 in. (2.54 cm.) in diameter, equally spaced, in each of the two narrow sides, and with a slot cut in one side for the vapor tube. The centers of these four openings are 8½ in. (21.59 cm.) below the top of the shield. There are also three ½-in. (1.27 cm.) holes in each of the four sides with their centers 1 in. (2.54 cm.) above the base of the shield.

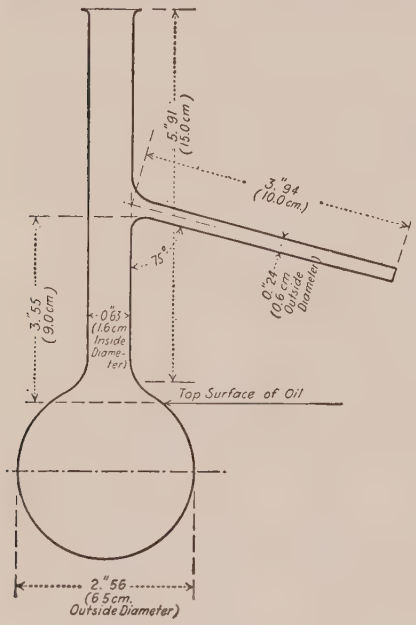


FIG. 240.—Dimensions of 100-ml. Engler Flask.

Ring Support and Hard Asbestos Boards.—The ring support is of the ordinary laboratory type, 4 in. (10.16 cm.) or larger in diameter, and is supported on a stand inside the shield. There are two hard asbestos boards: One 6 by 6 by ¼ in. (15.24 by 15.24 cm. by 6.35 mm.) with a hole 1¼ in. (3.18 cm.)[7] in diameter in its center, the sides of which shall be perpendicular to the surface; the other, an asbestos board to fit tightly inside the shield, with an opening 4 in. (10.16 cm.) in diameter concentric with the ring support. These are arranged as follows: The second asbestos board is placed on the ring and the first or smaller asbestos board on top so that it may be moved in accordance with the directions for placing the distilling flask. Direct heat is applied to the flask only through the 1¼-in. (3.18 cm.) opening in the first asbestos board.

Gas Burner or Electric Heater.—(*a*) *Gas Burner.*—The burner is so constructed that sufficient heat can be obtained to distill the product at the uniform rate specified below. The flame should never be so large that it spreads over a circle of diameter greater than 3½ in. (8.89 cm.) on the under surface of the asbestos board. A sensitive regulating valve is a necessary adjunct, as it gives complete control of heating.

(*b*) *Electric Heater.*—The electric heater, which may be used in place of the gas flame, shall be capable of bringing over the first drop within the time specified below when started cold, and of continuing the distillation at the uniform rate. The electric heater shall be fitted with an asbestos board top ⅛ to ¼ in.

[7] When distilling petroleum products having an end point above 470° F. (243.34° C.), the hole in the asbestos board shall be 1½ in. (3.81 cm.) in diameter.

(3.18 to 6.35 mm.) thick, having a hole 1¼ in. (3.18 cm.) in diameter in the center. When an electric heater is employed, the portion of the shield above the asbestos board shall be the same as with the gas burner but the part below the board may be omitted.

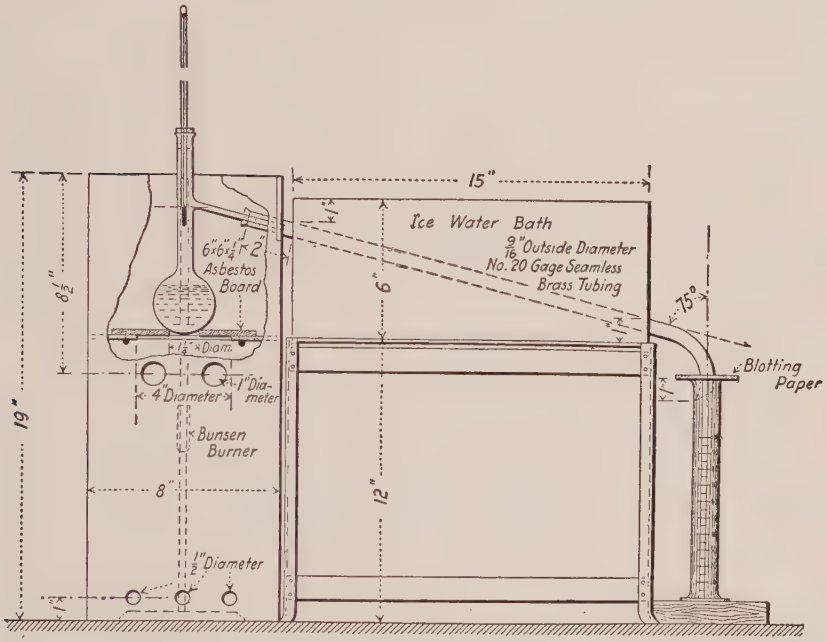


Fig. 241.—Apparatus for Distillation Test.

Thermometers.—(*a*) The A. S. T. M. Low-Distillation Thermometer shall conform to the following requirements. These specifications cover a total-immersion thermometer graduated in either Centigrade or Fahrenheit degrees, as specified, the ranges being 0 to 300° C. or 30 to 580° F. respectively.

Type: Etched stem, glass.
Liquid: Mercury.
Range and Subdivision: 0 to 300° C. in 1° C. or 30 to 580° F. in 2° F.
Total Length: 378 to 384 mm. (14.88 to 15.12 in.).
Stem: Plain front, enamel back, suitable thermometer tubing.
Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).
Bulb: Corning normal or equally suitable thermometric glass.
Length, 10 to 15 mm. (0.39 to 0.59 in.).
Diameter, 5.0 to 6.0 mm. (0.20 to 0.24 in.).
Distance to 0° C. or 32° F. Line from Bottom of Bulb: 100 to 110 mm. (3.94 to 4.33 in.).
Distance to 300° C. or 572° F. Line from Top of Thermometer: 30 to 45 mm. (1.18 to 1.77 in.).
Filling above Mercury: Nitrogen gas.
Top Finish: Glass ring.

GRADUATION: All lines, figures, and letters clear cut and distinct. The first and each succeeding 5° C. or 10° F. line to be longer than the remaining lines. Graduations to be numbered at each multiple of 10° C. or 20° F.

IMMERSION: Total.

SPECIAL MARKING: "A. S. T. M. Low Distillation," a serial number and the manufacturer's name or trade mark shall be etched on the stem.

SCALE ERROR: The error at any point of the scale when the thermometer is standardized as provided below shall not exceed 0.5° C. or 1° F.

STANDARDIZATION: The thermometer shall be standardized immersed in the testing bath to the top of the mercury column, at the ice point and at temperature intervals of approximately 50° C. or 100° F. up to 300° C. or 572° F.

TEST FOR PERMANENCY OF RANGE: After being subjected to a temperature of 280 to 290° C. or 540 to 560° F. for 24 hours, the accuracy shall be within the limit specified. The test shall be made under the immersion conditions specified for this thermometer.

CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. Low Distillation, 0 to 300° C." or "A. S. T. M. Low Distillation, 30 to 580° F." according to the type of thermometer.

NOTE 1.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

(*b*) The A. S. T. M. High-Distillation Thermometer shall conform to the following requirements. These specifications cover a total-immersion thermometer graduated either in Centigrade or Fahrenheit degrees, as specified, the ranges being 0 to 400° C. or 30 to 760° F., respectively.

TYPE: Etched stem, glass.

LIQUID: Mercury.

RANGE AND SUBDIVISION: 0 to 400° C. in 1° C. or 30 to 760° F. in 2° F.

TOTAL LENGTH: 378 to 384 mm. (14.88 to 15.12 in.).

STEM: Plain front, enamel back, suitable thermometer tubing. Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).

BULB: Corning normal or equally suitable thermometric glass.
Length, 10 to 15 mm. (0.39 to 0.59 in.).
Diameter, 5.0 to 6.0 mm. (0.20 to 0.24 in.).

DISTANCE TO 0° C. OR 32° F. LINE FROM BOTTOM OF BULB: 25 to 35 mm. (0.98 to 1.38 in.).

DISTANCE TO 400° C. OR 752° F. LINE FROM TOP OF THERMOMETER: 30 to 45 mm. (1.18 to 1.77 in.).

FILLING ABOVE MERCURY: Nitrogen gas.

TOP FINISH: Glass ring.

GRADUATION: All lines, figures and letters clear cut and distinct. The first and each succeeding 5° C. or 10° F. line to be longer than the remaining lines. Graduations to be numbered at each multiple of 10° C. or 20° F.

IMMERSION: Total.

SPECIAL MARKING: "A. S. T. M. High Distillation" a serial number and the manufacturer's name or trade mark shall be etched on the stem.

SCALE ERROR: The error at any point of the scale up to 370° C. or 700° F. when the thermometer is standardized as provided below shall not exceed 1° C. or 2° F.

STANDARDIZATION: The thermometer shall be standardized immersed in the testing bath to the top of the mercury column, at the ice point and at temperature intervals of approximately 50° C. or 100° F. up to 370° C. or 700° F.

TEST FOR PERMANENCY OF RANGE: After being subjected to a temperature between 360 and 370° C. or 680 and 700° F. for 24 hours, the accuracy shall be within the limit specified. The test shall be made under the immersion conditions specified for this thermometer.

CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. High Distillation, 0 to 400° C." or "A. S. T. M. High Distillation, 30 to 760° F." according to the type of thermometer.

NOTE 1.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

NOTE 2.—Under certain test conditions, the bulb of the thermometer may be 50° F. (28° C.) above the temperature indicated by the thermometer, and at an indicated temperature of 700° F. (371° C.) the temperature of the bulb is approaching a critical range in the glass. It is therefore not desirable to use this thermometer under such conditions at indicated temperatures above 700° F. (371° C.) without checking the ice point.

Graduate.—The graduate shall be of the cylindrical type, of uniform diameter, with a pressed or molded base and a lipped top. The cylinder shall be graduated to contain 100 ml., and the graduated portion shall be not less than 7 in. (17.78 cm.) nor more than 8 in. (20.32 cm.) long. It shall be graduated in single milliliters and each fifth mark shall be distinguished by a longer line. It shall be numbered from the bottom up at intervals of 10 ml. The overall height of the graduate shall be not less than 9¾ in. (24.8 cm.), nor more than 10¼ in. (26.0 cm.). The graduations shall not be in error by more than 1 ml. at any point on the scale.

Procedure.—(*a*) The condenser bath shall be filled with cracked ice,[8] and enough water added to cover the condenser tube. The temperature shall be maintained between 32 and 40° F. (0 and 4.45° C.).

(*b*) The condenser tube shall be swabbed to remove any liquid remaining from the previous test. A piece of soft cloth attached to a cord or copper wire may be used for this purpose.

(*c*) One hundred milliliters of the product shall be measured in the 100-ml. graduated cylinder at 55 to 65° F. (12.8 to 18.3° C.) and transferred directly to the Engler flask. None of the liquid shall be permitted to flow into the vapor tube.

(*d*) The thermometer (Note) provided with a cork shall be fitted tightly into the flask so that it will be in the middle of the neck and so that the lower end of the capillary tube is on a level with the inside of the bottom of the vapor outlet tube at its junction with the neck of the flask. The thermometer shall be approximately at room temperature when placed in the flask.

NOTE.—For products having end points not higher than 482° F. (250° C.) or initial boiling points not higher than 212° F. (100° C.), the Low-Distillation Thermometer shall be used; for products having end points higher than 482° F. (250° C.) and initial boiling points higher than 212° F. (100° C.) the High-Distillation Thermometer shall be used.

[8] Any other convenient cooling medium may be used.

(*e*) The charged flask shall be placed in the 1¼-in. (3.18-cm.) opening in the 6 by 6-in. (15.24 by 15.24-cm.) asbestos board with the vapor outlet tube inserted into the condenser tube. A tight connection may be made by means of a cork through which the vapor tube passes. The position of the flask shall be so adjusted that the vapor tube extends into the condenser tube not less than 1 in. (2.54 cm.) nor more than 2 in. (5.08 cm.).

(*f*) The graduated cylinder used in measuring the charge shall be placed, without drying, at the outlet of the condenser tube in such a position that the condenser tube shall extend into the graduate at least 1 in. (2.54 cm.) but not below the 100-ml. mark. Unless the temperature is between 55° and 65° F. (12.8° and 18.3° C.) the receiving graduate shall be immersed up to the 100-ml. mark in a transparent bath maintained between these temperatures. The top of the graduate shall be covered closely during the distillation with a piece of blotting paper or its equivalent, cut so as to fit the condenser tube tightly.

When everything is in readiness, heat shall be applied at a uniform rate, so regulated that the first drop of condensate falls from the condenser in not less than 5 nor more than 10 minutes. The distillation thermometer shall be read 2 minutes after heat is applied and the indication recorded as the "correction temperature." This figure is of significance only in cases when there is a question as to the accuracy [9] of the initial boiling point, as subsequently determined. When the first drop falls from the end of the condenser the reading of the distillation thermometer shall be recorded as the *initial boiling point.* The receiving cylinder shall then be moved so that the end of the condenser tube shall touch the side of the cylinder. The heat shall then be so regulated that the distillation will proceed at a uniform rate of not less than 4 nor more than 5 ml. per minute. The volume of distillate collected in the cylinder shall be observed and recorded, to the nearest 0.5 ml., when the mercury of the thermometer reaches each point that is a multiple of 10° C. or the Fahrenheit equivalent of this point (30° C., 40° C., 50° C., 60° C., etc., or 86° F., 104° F., 122° F.,

[9] The initial boiling point is one of the observations which it is customary to report as indicative of the quality of gasoline. It is a point which is very difficult to check, especially when duplicate tests are made at different room temperatures, and it has not been found practical to devise an accurate method of correcting for this unavoidable variation in operating conditions. The practical significance of initial boiling point is not regarded as sufficient to warrant requiring that tests be conducted under regulated conditions of room temperature. The following directions are included as an expedient intended to obviate some of the difficulties that develop on account of the practice of including initial boiling point limits in specifications for the purchase and sale of gasoline:

If the "correction temperature" is below 70° F. (21° C.) or above 80° F. (27° C.), the observed initial boiling point, if it is below 150° F. (66° C.), may be considered incorrect by an amount not less than one third the difference between the "correction temperature" and 75° F. (24° C.). In case there is a dispute between buyer and seller, the observed initial boiling point figures obtained by all parties shall be revised according to the following formula:

$$\text{Revised initial boiling point} = \left\{\begin{matrix}\text{observed initial}\\ \text{boiling point}\end{matrix}\right\} - \frac{\text{Correction Temperature (deg. Fahr.)} - 75}{3}$$

If all of the revised figures fall within the specification limit the gasoline in question shall be considered as passing; otherwise arrangements shall, if possible, be made to conduct a distillation test with the room temperature maintained between the limits of 70 and 80° F. (21 and 27° C.), inclusive.

140° F., etc.). If preferred, the reading of the distillation thermometer may be observed and recorded when the level of the distillate reaches each 10-ml. mark on the graduate. In case a product is being tested to ascertain whether or not it conforms with a given specification, all necessary observations shall be made and recorded, whether or not they are included in the series ordinarily employed by the laboratory making the test.

No adjustment of the heat shall be made after the liquid residue in the flask is approximately 5 ml. unless the time required to bring over the last 5 ml. of distillate and reach the end point exceeds 5 minutes. The end point is the maximum temperature observed on the distillation thermometer and is usually reached after the bottom of the flask has become dry. If the bottom of the flask is not dry the operator shall record this fact.

In case the time required to bring over the last 5 ml. of distillate and reach the end point exceeds 5 minutes the test shall be repeated and the heat shall be adjusted when the liquid residue reaches 5 ml. This adjustment may be either an increase or a decrease but must accomplish the purpose of bringing the period required to vaporize the last 5 ml. of distillate and reach the end point within the limits of 3 and 5 minutes.

The total volume of the distillate collected in the receiving graduate shall be recorded as the *recovery*.

The cooled residue shall be poured from the flask into a small cylinder graduated in 0.1 ml., measured when cool and the volume recorded as *residue*.

The difference between 100 ml. and the sum of the recovery and the residue shall be calculated and recorded as *distillation loss*.

Accuracy.—With proper care and attention to detail, duplicate results obtained for initial boiling point and end point, respectively, should not differ from each other by more than 6° F. (3.3° C.). Duplicate readings of the volume of distillate collected in the cylinder when each of the prescribed temperature points is reached should not differ from each other by more than 2 ml. In case observations are made on the basis of prescribed percentage points, the differences in temperature readings should not exceed the amounts equivalent to 2 ml. of distillate at each point in question.

Correction for Barometric Pressure.—The actual barometric pressure shall be ascertained and recorded, but no correction shall be made except in case of dispute. In such cases the temperature points shall be corrected to 760 mm. (29.92 in.), by the use of the Sydney Young equation, as follows:

For Centigrade readings:

$$C_c = 0.00012(760 - P)(273 + t_c)$$

For Fahrenheit readings:

$$C_f = 0.00012(760 - P)(460 + t_f)$$

in which C_c and C_f are, respectively, corrections to be added to the observed temperature t_c or t_f, and P is the actual barometric pressure in millimeters of mercury.

The following table is a convenient approximation of the corrections as calculated by the above equation.

Temperature Range		Correction [10] per 10-mm. Difference in Pressure	
Deg. Cent.	Deg. Fahr.	Deg. Cent.	Deg. Fahr.
10– 30	50– 86	0.35	0.63
30– 50	86–122	0.38	0.68
50– 70	122–158	0.40	0.72
70– 90	158–194	0.42	0.76
90–110	194–230	0.45	0.81
110–130	230–266	0.47	0.85
130–150	266–302	0.50	0.89
150–170	302–338	0.52	0.94
170–190	338–374	0.54	0.98
190–210	374–410	0.57	1.02
210–230	410–446	0.59	1.06
230–250	446–482	0.62	1.11
250–270	482–518	0.64	1.15
270–290	518–554	0.66	1.19
290–310	554–590	0.69	1.24
310–330	590–626	0.71	1.28
330–350	626–662	0.74	1.32
350–370	662–698	0.76	1.37
370–390	698–734	0.78	1.41
390–410	734–770	0.81	1.45

Significance of the Test.—The lighter portions, for example, those between 150° and 200°, burn much better than those between 250° and 290°; the heavy portions of American petroleum burn much better than those of the Russian oils.

The end point shall not be higher than 625° F. For lighthouse kerosene (the highest grade) the U. S. requirements are as follows: first drop not lower than 160° C.; 10% over below 175°, 90% over below 270°, end-point not higher than 280° and 97% recovered as distillate in the receiver.

The averages from four samples of Caucasian and ten samples of American oils subjected to this test were as follows, in per cent by volume: [1]

	Below 150° C.	150–290° C.	Above 290° C.
Caucasian petroleum	8.0	86.6	5.4
American petroleum	16.9	57.1	26.0

The portion boiling below 150° C. is by some regarded as the gasoline or naphtha portion of the kerosene.

Determination of Sulfur.—The deleterious effect of the oxides of sulfur upon hangings and bindings—as well as upon the human system—is well known, sulfuric acid being their ultimate product. The sulfur exists in combination, partly as compounds formed from the sulfuric acid used in refining and partly as alkyl sulfides. Its qualitative detection may be effected by heating the oil to its boiling-point with a bright piece of sodium or potassium. If

[10] To be added in case barometric pressure is below 760 mm.; to be subtracted in case barometric pressure is above 760 mm.

sulfur compounds be present, a yellowish layer is formed upon the metal. After cooling add distilled water drop by drop until the metal is dissolved, and test for sulfides with sodium nitroprusside.

TENTATIVE METHOD OF TEST FOR SULFUR IN PETROLEUM OILS BY LAMP METHOD [11]

A. S. T. M. Designation: D 90–34 T [12]

This method shall be used for the determination of sulfur in kerosene, petroleum naphtha, and other petroleum oils which can be burned completely in a wick lamp. This method may be applied to motor fuels which are mixtures of gasoline and volatile non-petroleum oils.

Note.—When this method is applied to mixtures containing carbon bisulfide approximately 85 per cent of the sulfur present as carbon bisulfide is usually determined.

Apparatus.—The apparatus shall consist of the following: (*a*) ***Absorber.***—An absorber of chemically-resistant glass conforming to the dimensions shown in Fig. 242. The larger of the two bulbs of the absorber shall be filled at least two-thirds full with pieces of chemically-resistant glass rod from 8 to 10 mm. in length and from 5 to 6 mm. in diameter, or with perforated beads of chemically resistant glass 5 to 8 mm. in diameter.

(*b*) ***Chimney.***—A chimney of chemically-resistant glass conforming to the dimensions shown in Fig. 242, and connected with the absorber by a cork stopper.

(*c*) ***Spray Trap.***—A spray trap of chemically-resistant glass conforming to the dimensions shown in Fig. 242, and connected with the absorber by a cork or by a rubber stopper.

(*d*) ***Lamp.***—A small lamp of about 25-ml. capacity. The lamp may conveniently consist of a 25 to 35-ml. Erlenmeyer flask, preferably of the shape shown in Fig. 242, and a cork carrying a piece of glass tubing 40 mm. in length, from 6 to 7 mm. in outside diameter, and 3 mm. in inside diameter, with ends ground or fused level. The wick tube should project above the cork at least 10 mm., and the cork shall have a vertical groove in its side so that air may enter the flask to replace the oil as it is consumed.

(*e*) ***Cotton Wicking.***—Two strands of clean, unused cotton wicking, 10 to 12 cm. in length and weighing about 5 to 6 mg. per cm. per strand.

(*f*) ***Filter Pump.***—A filter pump or other means for continuous suction.

Solutions Required: (*a*) ***Hydrochloric Acid.***—Prepare a solution of HCl in distilled water which will contain 2.275 g. of HCl per liter and check carefully for accuracy.

[11] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[12] This is a Tentative Standard and under the Regulations of the Society is subject to annual revision. Suggestions for revision should be addressed to the Headquarters of the Society, 260 S. Broad St., Philadelphia, Pa. Issued, 1921; Revised, 1924, 1926, 1929, 1930, 1934.

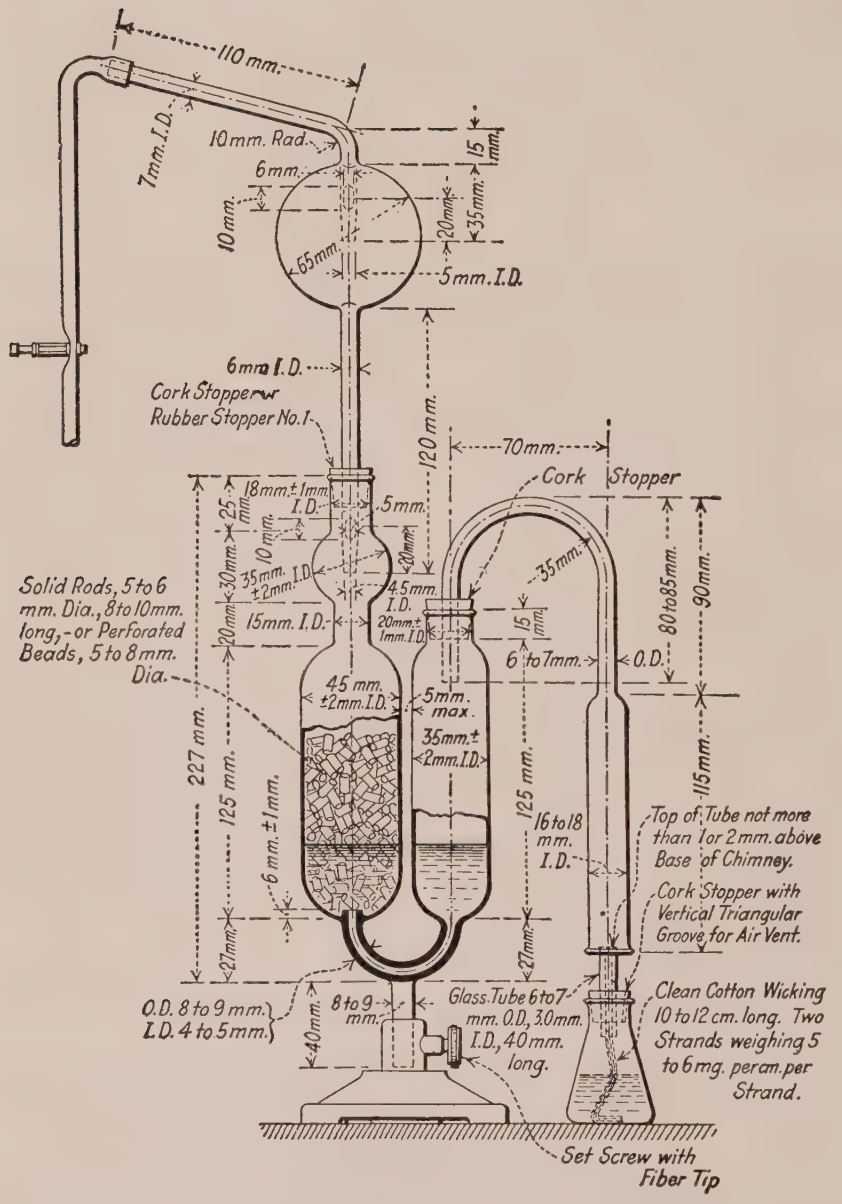


FIG. 242.—Apparatus for Determining Sulfur in Oils.

NOTE.—In the case of those dimensions for which no specific tolerance are designated above, the permissible variation is ± 10 per cent to the nearest millimeter, provided, however, that in no case the deviation be greater than 5 mm.

(*b*) ***Sodium Carbonate.***—Dissolve 3.306 g. of Na_2CO_3 in one liter of distilled water. Ten milliliters of this solution should neutralize exactly 10 ml. of the HCl solution.

(*c*) ***Methyl Orange.***—Dissolve 0.004 g. of methyl orange in one liter of distilled water.

Procedure.—The sulfur shall be determined as follows:

(*a*) Pass two strands of the new cotton wicking through the wick tube so that they are not twisted but are parallel in the wick tube. Pour into the clean, dry lamp about 15 ml. of the oil to be tested, and insert the cork containing the wick tube. After the wick has become saturated with the oil, trim it off as nearly as possible to the top of the wick tube with a pair of sharp scissors, finally adjusting the wick height by touching the top of it with the tip of a finger. Weigh the oil and lamp assembly to the nearest 0.001 g. Run a blank determination at the same time and under the same conditions by burning sulfur-free alcohol in a similar lamp. Thoroughly rinse out the absorber with distilled water, and put into it exactly 10 ml. of the sodium carbonate solution from an accurately calibrated pipette, and then dilute the solution with 10 ml. of distilled water. Rinse out also the chimney and the spray trap with distilled water, dry the chimney, and connect both to the absorber as shown in Fig. 242. Prepare the apparatus for the blank determination in the same manner, putting into it exactly 10 ml. of the sodium carbonate solution and 10 ml. of distilled water. Apply gentle suction to both absorbers; light both the oil lamp and the alcohol lamp and then place them in position under the chimneys so that the top of each wick tube extends into the chimney not more than 1 or 2 mm. above the edge. Use a sulfur-free flame, such as an alcohol lamp for lighting the lamps; do not use matches. Adjust the suction so that a steady flame 12 to 18 mm. in height and free from smoking is obtained (Note 1). The suction shall be adjusted so that air is drawn through both absorbers at approximately the same rate. The maintenance of proper flame height usually requires that the wick be flush with the top of the wick tube for naphthas or motor fuels and a little higher for illuminating oils. The room shall be free from draughts. Continue burning for from one to one and one-half hours, or less if the sulfur content of the oil is high. During this time the oil should be consumed at the rate of about 2 to 2.5 g. per hour.

(*b*) Extinguish the flames and stop the suction on both absorbers. Weigh the oil lamp immediately to the nearest 0.001 g., and determine by difference the weight of oil consumed. Working with the blank first, disconnect the spray trap and chimney and wash them thoroughly with the methyl orange solution, using a wash bottle with a very fine jet and collecting the washings in the absorber. Use approximately 35 ml. of the solution for washing. Carefully titrate the faintly-yellow solution with the HCl solution. During titration, carefully agitate the contents of the absorber either by alternate sucking and blowing through a rubber tube held between the lips, or else by the use of a suitable rubber-syringe bulb. As the end point is approached, draw the liquid back and forth between the bulbs after each addition of acid, agitating as before. When the first permanent pink color appears, the end point has been reached. Read and record the volume of HCl solution used (Note 2).

(*c*) Rinse the chimney and the spray trap used in the actual determination into the absorber to which they were connected, exactly as has been prescribed

for the blank. If at this point the solution in the absorber should have a pink color, too much oil has been burned and the determination shall be repeated, but burning for a shorter time. The temporary pink color that sometimes appears in the chimney when rinsing it out should be disregarded. Titrate just as in the blank, continuing to add the HCl solution until the color matches that obtained in the blank. Read and record the volume of HCl solution used.

NOTE 1.—If it is not possible to obtain a good flame free from smoking, as sometimes happens if the oil contains considerable percentages of benzol, dilute the oil with an equal weight of sulfur-free anhydrous alcohol before putting the sample into the lamp. If, while maintaining the specified flame height the flame still smokes, a smaller flame is permissible. In order to get the correct value when calculating the percentage of sulfur present in this case, allowance shall be made for the fact that the sample as burned in the lamp is one-half alcohol. This shall be done by doubling the percentage of sulfur obtained in computation by the formula given below.

NOTE 2.—For accurate work, conditions shall be such that a minimum or zero blank is obtained. If the titration of the blank requires more than 0.1 ml. of the HCl solution per gram of sample burned, which corresponds to 0.01 per cent of sulfur, a high degree of accuracy cannot be expected in the case of oils of low sulfur content.

Calculate the sulfur content of the oil by substituting the proper values in the following formula:

$$\text{Percentage of sulfur} = \frac{\text{milliliters of HCl for blank} - \text{milliliters of HCl for sample}}{\text{grams of oil burned} \times 10}$$

This formula is correct only for the standard solutions specified, pp. 1713, 1715, 1 ml. of each being equivalent to 0.001 g. of sulfur. The use of solutions of any other strength, such as 0.1 N, involves more complicated calculation and is not advisable.

As a check on the determination, a sample of known sulfur content shall be analyzed. Such a reference sample may be made by adding a pure volatile sulfur compound, such as carbon bisulfide, to sulfur-free anhydrous alcohol. This check shall indicate from 85 to 100% of the sulfur present.

Accuracy.—Duplicate determinations by the same operator should not differ by more than the amounts given in the following tabulation:

Sulfur Found, per cent	Average Deviation from Mean, per cent Sulfur
Under 0.125	0.0025
0.125 to 0.25	0.005
0.25 to 0.50	0.01
Over 0.50	0.02

For different operators corresponding deviations may be double those given above.

The barium sulfate can be precipitated and determined for rapid work by the Jackson Turbidimeter.

The percentage of sulfur in a kerosene should not exceed 0.05; the Pennsylvania oils contain usually 0.02 to 0.03, the Lima 0.04 to 0.05.[13]

Detection of Acidity.—Shake equal quantities of oil and warm water in a test-tube, pour off the oil, and test the water with litmus paper. If the water be strongly acid, the quantity may be determined as in "Free Acid," page 1782.

[13] Kissling, Ch., Rev. Fett und Harz. Ind., **14**, 157, 1906.

The acid in this case is most probably sulfuric, coming from the refining process.

Sulfuric Acid Test.—The object of this test is to judge of the degree of refinement of the oil, a perfectly refined oil giving little or no color when submitted to the process. One hundred grams of oil and 40 grams of sulfuric acid, 1.73 specific gravity, are shaken together for two minutes in a glass-stoppered bottle and the color of the acid noticed. For comparative work this color is matched by solutions of Bismarck brown.[14]

Mineral Salts.—Salts of calcium or magnesium when dissolved in the oil diminish its illuminating power; their action is to form a crust on the wick and prevent access of air.

Redwood [15] states that 0.02 gram of either of these salts in 1000 grams of oil diminishes the illuminating power 30 to 40% in eight hours.

They are determined by distilling 100 to 200 ml. of the oil down to about 20 ml., evaporating and igniting this residue, and subsequently treating with hydrochloric acid. The calcium and magnesium are then determined in the usual way.

Determination of Water.—By rubbing the oil together with a little eosin on a glass plate the oil will take on a pink color if water be present.

The evaporation method is approximate and applicable only to heavy oils and greases. Its accuracy even with heavy greases is questionable.

Dilute [16] the oil with an equal volume of benzol, whirl it vigorously in a centrifuge until the separated layer of water does not appear to increase in volume. However, as water is somewhat soluble in any diluent used and also in oils, a portion of the water content will fail to appear, consequently the method in which a diluent is used cannot be considered accurate. It is advisable first to agitate the diluent vigorously with water and then to separate with the centrifuge in order to saturate it with water before using. See also Dean's test under Fuel Oil.

Groschuff [17] states that 100 grams of benzene will dissolve 0.03 gram of water at 3° C. and 0.337 gram of water at 77° C., whereas petroleum products (density 0.792) will dissolve from 0.0012 gram at 2° C. to 0.097 gram at 94° C.

While water to the extent even of 3 or 4% is apparently without influence on the viscosity, 1% extinguishes the flame when making the flash test.

Color.—This test has lost its importance, since oils are sometimes satisfactory despite their yellow color. The determination is usually made with the Saybolt colorimeter,[18] in which the depth of the oil is changed in a cylinder until it matches the color of standard plates of uranium glass.

(b) Lubricating Oils

The tests to be made are, in the order of their importance, viscosity, specific gravity, evaporation, cold test, pour point, flash test, fire test, test for soap, carbon residue test, friction test. Saponification value, tarry matter insoluble in 88° naphtha, color and added impurities are also determined.

[14] J. Soc. Chem. Ind., **15**, 678, 1896.
[15] Dingler, Pol. J., **255**, 427, 1887.
[16] Reported by Allen and Jacobs. Bureau of Mines Technical Paper No. 25, 1912.
[17] Groschuff, Chem. Abs., **5**, 2550, 1911.
[18] Tech. Paper 323B.

The office of a lubricant is to prevent the attrition of axle and journal box by interposing itself between them in a thin layer, upon which the shaft revolves. The ideal lubricant is that which has the greatest adhesion to surfaces and the least cohesion among its own particles, or, as the practical man expresses it, the most fluid oil that will do the work and stay in place. The determination of its viscosity or " body " is then of the first importance.

Viscosity is the degree of fluidity of an oil or its internal friction. It is independent of the specific gravity of the oil, although this in the pipette instruments influences the time of efflux. Within certain limits it may be taken as a measure of the value of oil as a lubricant, by comparing the viscosity of the oil under examination with that of other oils which have been found to yield good results in practice.

The instruments employed for its determination may be divided into two classes—pipette viscosimeters, giving the time of efflux, as those of Engler, Saybolt, and others, and torsion viscosimeters, giving the retardation due to the oil, those of MacMichael and Doolittle.

In expressing viscosity, consequently, it is necessary to give the name of the instrument with which it is determined. It is sometimes expressed as specific viscosity, that is, the time of the oil divided by the time of water; this is only comparative when done with instruments of the same name, that is, specific viscosity Engler is not the same figure as specific viscosity Saybolt. Besides this manner of expressing viscosity, it is measured in absolute (C.G.S.) units or dynes per cm. This unit of viscosity has received the name of Poise from Poiseuille, one of the first to express this property in absolute measure. This is possible when the diameter of the orifice, its length, the quantity and specific gravity of the oil, its time of efflux and change of head are known. Where it is impracticable to determine all these data by direct measurements, the readings of a viscosimeter may be changed into dynes by determining the viscosity in seconds of standard solutions of glycerine, the viscosity of these being determined in dynes from tables of physical constants. Or it may be done by use of the tables on pages 1726 and 1799.

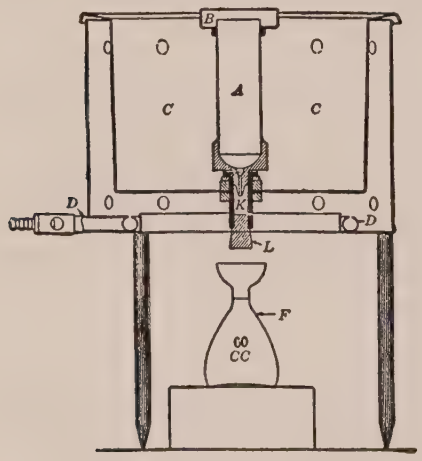


Fig. 243.—Engler Viscosimeter.

Engler Apparatus. — *Description.* The apparatus (Fig. 243) consists of a flat, brass cylindrical vessel, *A*, 106 mm. in diameter and about 62 mm. deep, holding 240 ml., provided with a jet 2.9 mm. in diameter and 20 mm. long. This vessel is gilt inside and the jet, in the standard instruments, is of platinum —ordinarily it is made of brass; the vessel is surrounded with a bath, *B*, either of water or oil, provided with a stirrer and heated by a ring burner. The jet is closed by the wooden valve, *F*, passing through the cover, and a thermometer, *c*, shows the temperature of the oil; three studs show the height to which *A* is

filled and at the same time when it is level. The oil ordinarily is discharged into the 200-ml. flask, although in case the oil or time be limited, 100 or 50 ml. may be used and the time of efflux multiplied by a suitable factor. The instrument is standardized with water, 200 ml. of which at 20° C. should run out in from 50 to 52 seconds.

Manipulation.—The instrument is thoroughly cleaned with alcohol and ether if necessary and dried; any suspended matter is removed from the oil, which is poured into it up to the level of the studs, stirred until 20° C. is reached and the bath adjusted to the same temperature. The flask is placed beneath the orifice, the plug raised and the time required for 200 ml. of oil to flow out is noted; this is divided by the water value of the instrument and gives then relative or specific viscosity. If only 50 ml. are allowed to run out the time must be multiplied by 5, and if 100 ml., by 2.35. If only 50 ml. were put in and 40 ml. allowed to run out, multiply this time by 3.62 to obtain the time for 200 ml.; if 66 ml. and 50 ml. run out, multiply by 2.79.[19] If it be desired to express the viscosity in absolute measure (C.G.S. units) it can be done by reference to the table on page 1726. It should be noted that specific viscosity obtained with a different type of instrument, e.g., the Saybolt, is not the same as with the Engler.

STANDARD METHOD OF TEST FOR VISCOSITY BY MEANS OF THE SAYBOLT VISCOSIMETER[20]

A. S. T. M. Designation: D 88–36[21]

Scope.—(*a*) This method shall be used for determining the Saybolt viscosity of petroleum products and lubricants.

(*b*) The Saybolt Universal Viscosimeter shall be used only for oils with times of flow of more than 32 sec. There is no maximum limit to viscosity to be measured by the Saybolt Universal Viscosimeter but, in general, liquids having an outflow time of the order of 1000 sec. and higher, Saybolt Universal, are tested more conveniently by means of the Saybolt Furol Viscosimeter.

(*c*) The Saybolt Furol Viscosimeter shall be used only for oils with times of flow of more than 25 sec. The outflow time of the Furol (Note) instrument is approximately one-tenth that of the Universal.

Note.—The word "Furol" is a contraction of the phrase "fuel and road oils."

Apparatus.—The apparatus shall consist of an oil tube, bath, receiver, thermometers, timer, and withdrawal tube, conforming to the requirements specified in the following Paragraphs (*a*) to (*g*):

[19] Gans, Chem. Revue der Fett und Harz. Ind., **6**, 221, 1899.

[20] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[21] This method is issued under the fixed designation D 88; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1921; Adopted in Amended Form, 1926; Revised, 1930, 1933, 1936.

(*a*) ***Oil Tube.***—The oil tube (illustrated in Fig. 244) shall be entirely of corrosion-resistant metal, with or without plating, and shall conform to the dimensional requirements shown in Table I within the permissible variations prescribed. The lower end of the oil tube shall be provided with a nut for locking it in place in the bath and with a cork or other suitable device to prevent flow until the test is started. For convenience a string or its equivalent may be attached to the cork for rapid removal.

The oil tube shall be standardized, and any correction in excess of 0.2% shall be applied. The time of flow shall be within ±1% (Note 1) of the time as obtained with the National Bureau of Standards' master Saybolt oil tube (Note 2).

NOTE 1.—For routine testing, oil tubes having corrections as high as ±2% may be employed, provided, however, that any new oil tubes obtained after the adoption of this method shall not have corrections higher than ±1%. For referee testing, oil tubes having corrections higher than ±1% shall not be employed.

The oil may be standardized by any one of the following methods:

(*a*) Determination of outflow time for American Petroleum Institute oil standard and application of appropriate correction to obtain established value for the oil standard.

(*b*) Calibration by National Bureau of Standards subsequent to January 1, 1935.

(*c*) Comparison with a tube certified by the National Bureau of Standards subsequent to January 1, 1935, provided the tube shows no evidence of damage or injury since certification.

NOTE 2.—This tube, conforming to the A. S. T. M. dimensional specifications, has outflow times calibrated against oil standards under the maintenance of the American Petroleum Institute Committee on Viscosity Standards.

TABLE I.—DIMENSIONS OF OIL TUBES

Dimensions	Saybolt Universal Viscosimeter			Saybolt Furol Viscosimeter		
	Minimum, cm.	Normal, cm.	Maximum, cm.	Minimum, cm.	Normal, cm.	Maximum, cm.
Inside diameter of outlet tube	0.1750	0.1765	0.1780	0.313	0.315	0.317
Outside diameter of outlet tube at lower end	0.28	0.30	0.32	0.40	0.43	0.46
Length of outlet tube [a]	1.215	1.225	1.235	1.215	1.225	1.235
Height of overflow rim above bottom of outlet tube [a]	12.40	12.50	12.60	12.40	12.50	12.60
Outside diameter of overflow rim, at the top [a, c]	[b]	—	3.30	[b]	—	3.30
Diameter of container [a]	2.955	2.975	2.995	2.955	2.975	2.995
Depth of cylindrical part of container [a]	8.8	—	—	8.8	—	—
Diameter of container between bottom of cylindrical part of container and top of outlet tube [a]	0.9	—	—	0.9	—	—

[a] This dimension is identical in the Saybolt Universal and the Saybolt Furol instruments.
[b] The minimum value shall preferably be not less than 3.2 cm.
[c] The section of overflow rim shall be bounded by straight lines, except that a fillet is permissible at the junction with the bottom of the gallery.

(*b*) ***Bath.***—The bath shall serve as a support to hold the oil tube in a vertical position and as a container for the bath liquid. The bath shall be equipped with a stirring device and with means for heating or cooling. The source of heat or refrigeration shall be more than 1¼ in. (3 cm.) from the oil tube. If an external heater is used it must be more than 2 in. (5 cm.) from the oil tube.

The bath temperature necessary to maintain thermal equilibrium (while the oil in the oil tube is well stirred by the oil-tube thermometer) shall be within ±0.1° F. (0.06° C.) of the standard temperatures of 70° F. (21.1° C.) or 77° F. (25° C.) or shall not exceed 100.25°, 122.35°, 130.5°, 141.0°, 181.5° or 212.0° F. (37.9°, 50.2°, 54.7°, 60.6°, 83.1° or 100.0° C.), respectively, for the standard temperatures mentioned in Section 3. The level of the bath liquid shall not be lower than ¼ in. (0.5 cm.) above the overflow rim of the oil tube. For referee testing the bath liquid must be one which in the bath used will meet the preceding bath-temperature conditions (Note).

NOTE.—These temperature requirements can be met with water, aqueous solutions, and some baths with oil. In routine testing oil is generally used as the bath medium. This is allowable provided the temperature of the oil bath is adjusted so that the necessary condition of thermal equilibrium is maintained. It may be necessary to maintain the oil bath at slightly higher temperatures than those specified in the preceding paragraph. Temperature differentials between oil bath and oil tube necessary to maintain thermal equilibrium may be double those given above.

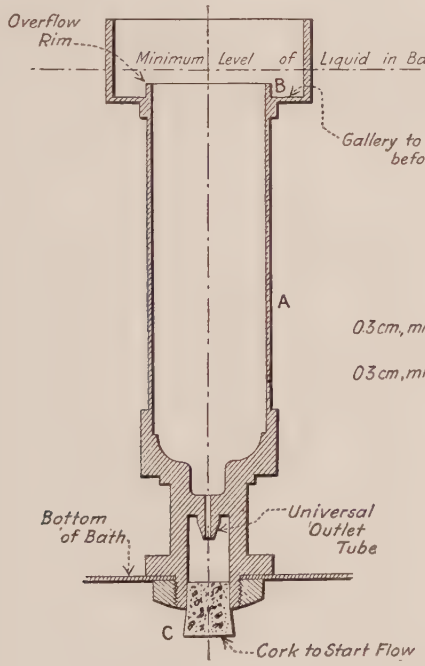


FIG. 244.—Sectional View of Standard Oil Tube.

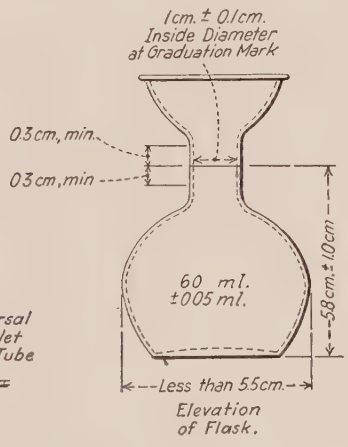


FIG. 245.—Receiving Flask. (This type of flask is recommended as convenient and durable.)

(*c*) ***Receiver.***—The receiving flask (see Fig. 245) shall be of glass with a capacity up to the graduation mark on its neck of 60 ml. ±0.05 ml. at 68° F. (20° C.). At the graduation mark, the inside diameter of the neck of the flask shall be 1 cm. ±0.1 cm. The cylindrical portion of the neck of the flask shall

extend not less than 0.3 cm. above and below the graduation mark. The graduation mark shall be 5.8 cm.±1.0 cm. above the bottom of the flask. The maximum outside diameter shall be less than 5.5 cm.

(*d*) ***Oil-Tube Thermometers.***—The oil-tube thermometers shall conform to the following requirements. They shall include two sets of six thermometers each, one set being graduated in Fahrenheit degrees and the other in Centigrade degrees, the ranges being chosen to include the temperatures commonly used in testing. To prevent contact of the thermometer with the orifice in the oil tube a suitable support shall be attached to the enlargement of the thermometer stem.

TYPE: Etched stem, glass.
LIQUID: Mercury.
RANGES AND SUBDIVISIONS:

Range	66° to 80° F.,	subdivisions in	0.2° F.	for tests at	70° and 77° F.
"	94° to 108° F.,	"	"	"	"	"	"	100° F.
"	120° to 134° F.,	"	"	"	"	"	"	122° and 130° F.
"	134° to 148° F.,	"	"	"	"	"	"	140° F.
"	174° to 188° F.,	"	"	"	"	"	"	180° F.
"	204° to 218° F.,	"	"	"	"	"	"	210° F.

or

Range	19° to 27° C.,	subdivisions in	0.1° C.	for tests at	21.1° and 25° C.
"	34° to 42° C.,	"	"	"	"	"	"	37.8° C.
"	49° to 57° C.,	"	"	"	"	"	"	50° and 54.4° C.
"	57° to 65° C.,	"	"	"	"	"	"	60° C.
"	79° to 87° C.,	"	"	"	"	"	"	82.2° C.
"	95° to 103° C.,	"	"	"	"	"	"	98.9° C.

TOTAL LENGTH: 252 to 256 mm. (9.92 to 10.08 in.).
STEM: Plain front, enamel back, suitable thermometer tubing. Diameter, 6 to 7 mm. (0.236 to 0.275 in.). The stem shall be made with an enlargement not less than 4 nor more than 7 mm. (0.16 to 0.28 in.) in length, having a diameter 2 to 3 mm. (0.08 to 0.12 in.) greater than that of the stem, the bottom of the enlargement being 114 mm. (4.5 in.) above the bottom of the bulb.
BULB: Corning normal or equally suitable thermometric glass.
Length, 25 to 35 mm. (1.0 to 1.4 in.).
Diameter, not less than 5 mm. (0.197 in.) and not greater than that of stem.
DISTANCE TO LOWEST SPECIFIED GRADUATION FROM BOTTOM OF BULB: 135 to 150 mm. (5.3 to 5.9 in.).
DISTANCE TO HIGHEST SPECIFIED GRADUATION FROM TOP OF THERMOMETER: 20 to 35 mm. (0.8 to 1.4 in.).
CONTRACTION CHAMBER: To be of long narrow type, top to be not more than 60 mm. (2.36 in.) above bottom of bulb, mercury to stand in contraction chamber at 32° F. (0° C.).
EXPANSION CHAMBER: To permit heating the thermometer 90° F. (50° C.) above highest temperature on scale, and in all cases to permit heating to 212° F. (100° C.).
FILLING ABOVE MERCURY: Nitrogen gas.
TOP FINISH: Glass ring.
GRADUATION: All lines, figures and letters clear cut and distinct. They shall be in black except for the special markings below. The first and each succeeding 1° F. or 0.5° C. line to be longer than the remaining lines. Graduations to be numbered at each multiple of 2° F. or 1° C.
IMMERSION: Total.
SPECIAL MARKING: The test temperatures specified in Section 3 shall be shown in full at the appropriate points on the thermometer scale; the graduations corresponding to the test temperatures and the numbers to be in red. A serial number and the manufacturer's name or trade mark shall be etched on the stem.
SCALE ERROR: The error at any point of the scale shall not exceed 0.2° F. (0.1° C.).

STANDARDIZATION: The thermometers are to be standardized for the condition of total immersion. Correction for emergent stem shall not be applied.
CASE: Each thermometer shall be supplied in a suitable case on which shall appear the marking, "A. S. T. M., Saybolt Viscosimeter Thermometer" and the range.

NOTE.—For the purpose of interpreting these specifications the following definitions apply:
The total length is the over-all length of the finished instrument.
The diameter is that measured with a ring gage.
The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.
The top of the thermometer is the top of the finished instrument.

(*e*) ***Bath Thermometers.***—Oil-tube thermometers, or other means for measuring temperature of at least equal accuracy, shall be used in the bath.

(*f*) ***Timer.***—The stop watch or other timing device used shall be graduated in divisions of 0.2 sec. or less, and shall be accurate to within 0.1% when tested over a 60-min. period (Note).

NOTE.—Electrical timing devices are permissible provided they are accurate and capable of being read to 0.2 sec. Timing devices actuated by synchronous motors shall be used only on electric circuits of controlled frequency.

(*g*) ***Withdrawal Tube.***—The tube or pipette used for draining the gallery shall have a smooth tip of about 3 mm. outside diameter and about 2 mm. inside diameter.

Temperature of Testing.—(*a*) With the Saybolt Universal Viscosimeter, determinations shall be made at 70°, 100°, 130° or 210° F. (21.1°, 37.8°, 54.4° or 98.9° C.).

(*b*) With the Saybolt Furol Viscosimeter, determinations shall be made at 77°, 100°, 122° or 210° F. (25°, 37.8°, 50° or 98.9° C.). In tests on road and paving materials, determinations may also be made at 140° and 180° F. (60° and 82.2° C.).

Procedure.—(*a*) Viscosity determinations shall be made in a room free from drafts and rapid changes in temperature. For standardization and referee tests the room shall be between 68° and 86° F. (20° and 30° C.) and the actual temperature shall be recorded. For routine tests, temperatures up to 100° F. may be employed without introducing errors in excess of 1%. Determinations shall not be made at temperatures below the dew point of the atmosphere surrounding the instrument.

(*b*) The oil tube shall first be cleaned with an effective solvent, such as benzol, and excess solvent shall be removed from the gallery.

(*c*) All oil shall be passed through a 100-mesh wire strainer before it is introduced into the oil tube. After the tube is cleaned, a quantity of the oil to be tested, sufficient to wet the entire surface of the tube, shall be poured into the tube and allowed to drain out (Note). The cork stopper shall be inserted not less than ¼ in. nor more than ⅜ in. into the lower end of the air chamber at the bottom of the oil tube. The cork shall fit tightly enough to prevent the escape of air, as evidenced by the absence of oil on the cork after it is withdrawn.

NOTE.—The plunger commonly supplied with the viscosimeter shall never be used on instruments maintained as standards.

(*d*) If the test temperature is above that of the room, the oil shall be heated to not more than 3° F. (1.7° C.) above the temperature of test and if the temperature is below that of the room, the oil shall be cooled to not more than 3° F. (1.7° C.) below the temperature of test. The oil shall be poured into the oil tube until it ceases to overflow into the gallery. The oil in the oil tube shall be kept well stirred with the oil-tube thermometer, care being taken to avoid hitting the outflow tube. The bath temperature shall be adjusted until the oil temperature remains constant. After thermal equilibrium has been attained no further adjustments shall be made in the bath temperature. The test results shall be discarded if the indicated bath temperature varies by more than ±0.05° F. (0.03° C.) in tests at 70°, 77°, 100°, 122° and 130° F. (21.1°, 25°, 37.8°, 50° and 54.4° C.) or by more than ±0.10° F. (0.06° C.) in tests at 140°, 180° and 210° F. (60°, 82.2° and 98.9° C.).

(*e*) After the temperature of the oil in the oil tube has remained constant within 0.02° F. (0.01° C.) of the desired temperature for 1 min. with constant stirring, the oil-tube thermometer shall be withdrawn and the surplus oil removed quickly from the gallery by means of the withdrawal tube so that the level of the oil in the gallery is below the level in the oil tube proper. The tip of the withdrawal tube shall be inserted at one point in the gallery. The test shall be started over again if the tip of the withdrawal tube touches the overflow rim (see Fig. 244). Under no conditions shall the excess oil be removed by rotating the withdrawal tube around the gallery.

(*f*) The receiving flask shall be placed in position so that the stream of oil from the outlet tube will strike the neck of the flask. The graduation mark on the receiving flask shall be not less than 10 cm. or more than 13 cm. from the bottom of the bath. The cork shall be snapped from its position and at the same instant the timer shall be started. The timer shall be stopped when the bottom of the meniscus of the oil reaches the mark on the neck of the receiving flask.

Reporting Results.—The time in seconds as determined by the prescribed procedure, with the proper calibration correction, is the Saybolt Universal (or Saybolt Furol) viscosity of the oil at the temperature at which the test is made. Results shall be reported to the nearest 0.1 sec. for viscosity values below 200 sec. and to the nearest whole second for values 200 sec. or above.

Accuracy.—With proper attention to details of method of procedure, results in different laboratories with different operators under referee or standardization conditions of testing, should not differ by more than 0.5%.

MacMichael's Viscosimeter.—This is an instrument of the torsion type in which a disk is suspended in a cup of fluid, the latter being rotated, and the torsion it produces on the disk noted. The disk is suspended by a gold-plated, steel wire 10 inches long, held between two grooved pins at the top of the standard. The brass cup is oil jacketed, the oil covering the wires ½ inch and heated electrically, or it may be cooled by ice or brine. A bent thermometer passing through the cover indicates the temperature, which may be controlled easily within a fraction of a degree. The graduated dial at the top of the disk is rotary and may be easily set to 0°. A dash pot filled with engine oil on the stem of the disk damps the action of the motor. In operating, the instrument is leveiled, the cup is filled to the mark with the fluid to be tested (about 100 ml.), the temperature adjusted, the cup rotated at about 20 R.P.M. and the readings

of the dial noted. These are in degrees of angular deflection, 300 to the circumference, and noted as ° M. = 1/1000 poise. Water at 20° should read 10° M. The smallest, or " practical unit " is 1° M.: by changing the decimal point, practical units, absolute units or specific viscosity may be obtained at one reading of the dial, no calculations being required. Three strengths of wire are supplied, giving water readings of 1°, 10°, and 100°, covering ranges of viscosity to 5000° M. or 5 poise.

The instrument should be calibrated by solutions of pure granulated sugar dried over sulfuric acid, the absolute viscosity of which is shown below. The accuracy of the instrument is well within 0.5%. The instrument is very rapid, the time required for a reading being very short. It can be applied to colloidal or lumpy solutions or suspensions, as limes, clay, glues, gums, explosives, paints, catsups or even jams with fruit seeds in them. The table below gives the wires applicable to different liquids.

CONSTANTS OF A SET OF TYPICAL WIRES

B. & S. Gauge No.	Diameter in Inches	Safe Limit Divisions M	Gm.-Cm. per M Division	Centipoises per M	Centipoises Range		Materials that Illustrate Range of Viscosities
					Minimum	Maximum	
22	.02535	125	.58905	2050	20000	256000	Heavy starch solutions, double boiled oils, rubber solutions
23	.02257	140	.3675	1280	12000	179000	
24	.02010	158	.2295	800	8000	126000	Putties, pastes and greases, viscose, single boiled oils, corn syrups, etc.
25	.01790	177	.13311	464	4500	82000	
26	.01594	199	.10557	368	3500	73300	
27	.01419	225	.05967	208	2000	46800	
30	.01002	315	.016065	56.0	500	17600	
32	.00795	398	.005355	18.7	180	6760	Raw starch, viscous oils, glycerin, etc.
34	.00630	503	.001836	6.4	60	3220	

VISCOSITY IN CENTIPOISES OF SUGAR SOLUTIONS[22]

Temp. 0° C.	Per cent Sugar by Weight			
	0	20	40	60
0	1.789	3.804	14.77	238
5	1.516	3.154	11.56	156
10	1.306	2.652	9.794	109.8
15	1.141	2.267	7.468	74.6
20	1.005	1.960	6.200	56.5
25	0.894	1.704	5.187	43.86
30	0.802	1.504	4.382	33.78

Absolute Viscosity.—This expresses viscosity in dynes, that is, the force necessary to produce the acceleration of 1 cm. per second on the mass of a gram.

[22] Bingham & Jackson, Bureau Standards Bulletin, No. 298 (1917).

It is independent of the instrument used; Engler numbers can be converted to absolute viscosity by the following factors:

Engler No.	Absolute Viscosity Dynes per Sq. Cm.[23]
1	0.01006 × specific gravity
2	0.1146 × specific gravity
5	0.353 × specific gravity
10	0.726 × specific gravity
20	1.46 × specific gravity
30	2.19 × specific gravity
60	4.38 × specific gravity

The Engler numbers of 5 or over are quite nearly proportional to the absolute viscosities.

Specific Gravity.—See under Burning Oils, page 1704.

Evaporation Test.[24]—The object of this test is to determine what percentage of an oil—more especially a spindle oil—is volatile when exposed to nearly the same conditions as it is on a bearing.

The oil is exposed upon annular disks of filter-paper $1\frac{5}{8}$ in. outside diameter, with hole $\frac{5}{8}$ in. in diameter, which have been standing in a sulfuric acid desiccator for several days, contained in a flat watch-glass.

Manipulation.—The watch-glass and paper are weighed—to tenths of a milligram—and about 0.2 gram of oil brought upon it by dropping from a rod, and *accurately* weighed. The watch-glass is now placed in an air bath, the temperature of which remains nearly constant at 60° to 65° C. (140° to 150° F.), and heated for eight hours. It is then cooled and reweighed, the loss being figured in per cent. No oil should be passed which gives an evaporation of more than 4%.

The following table of results upon some spindle oils shows the relation of gravity, flash point, and evaporation:

Gravity	Flash, ° F.	Evaporation	Gravity	Flash, ° F.	Evaporation
—	298	7.0%	.862	352	0.9%
.846	318	4.4%	.866	366	1.7%
—	348	2.0%	.870	384	0.8%
.852	348	1.0%	.882	364	1.7%
.856	336	1.4%			

Notes.—The temperature employed, 65° C., is approximately that attained by a bearing (in a spinning frame) after running two hours, thus leaving the oil exposed to it for eight hours, assuming a ten-hour day.

The test is important to the insurance underwriter, because it measures the amount of inflammable material sent into the air, and hence the liability to cause or aid conflagrations; it is important to the mill-owner, as it indicates the quantity of oil left upon the bearing, hence serving its purpose.

The test is made upon other oils by heating them six hours in a shallow dish to 100°, 150°, 220°, or 300°, sometimes in a draft of air or A. S. T. M. D 6-27 method as for road materials may be used.

[23] Waidner, Proc. Am. Soc. Test. Mat., Pt. I, 293, 1915.
[24] Archbutt, J. Soc. Chem. Ind., **15**, 326, 1896.

Cold Test.—This may be defined as the temperature at which the oil will just flow.

Manipulation.—A 4-oz. vial is one-fourth filled with the oil to be examined, a short, rather heavy, thermometer inserted in it, and the whole placed in a freezing mixture. When the oil has become solid throughout, let it stand one hour; the vial is removed, the oil allowed to soften, and thoroughly stirred until it will run from one end of the bottle to the other. The reading of the thermometer is now taken by withdrawing it and wiping off the oil with waste to render the mercury visible.

The chilling-point is the temperature at which flakes or scales begin to form in the liquid, and is determined similarly, by cooling the liquid 5° at a time.

STANDARD METHOD OF TEST FOR CLOUD AND POUR POINTS [25]

A. S. T. M. Designation: D 97–34 [26]

The cloud point of a petroleum oil is the temperature at which paraffin wax or other solid substances begin to crystallize out or separate from solution when the oil is chilled under definite prescribed conditions.

The pour point of a petroleum oil is the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under definite prescribed conditions.

The test for cloud point shall be used only for oils which are transparent in layers 1½ in. thick.

The test for pour point shall be used for all other petroleum oils and may be used for oils on which the test for cloud point is permitted.

Apparatus.—(See Fig. 246.) The test jar, *a*, shall be of clear glass, cylindrical form, flat bottom, approximately $1\frac{3}{16}$ to $1\frac{5}{16}$ in. in inside diameter and 4½ to 5 in. high. An ordinary 4-oz. oil sample bottle may be used if it is within the above specifications, and no test jar is available.

The thermometer, *b*, shall conform to the requirements of one of the following specifications:

(*a*) These specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −38 to +50° C. or −36° to +120° F., respectively.

Type: Etched stem, glass.
Liquid: Mercury.
Range and Subdivision: −38 to +50° C. in 1° C. or −36 to +120° F. in 2° F.

[25] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

This method comprises a revision of the Standard Method of Test for Cloud and Pour Points (A. S. T. M. Designation: D 97–33), 1933 Book of A. S. T. M. Standards, Part II, p. 761, which method it supersedes.

[26] This method is issued under the fixed designation D 97; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1921; Adopted in Amended Form, 1928; Revised, 1930, 1933, 1934. This method has been approved as American Standard by the American Standards Association.

Total Length: 220 to 224 mm. (8.69 to 8.81 in.).
Stem: Plain front, enamel back, suitable thermometer tubing. Diameter, 7.0 to 8.0 mm. (0.28 to 0.31 in.).
Bulb: Corning normal or equally suitable thermometric glass.
Length, not over 9.5 mm. (0.37 in.).
Diameter, not greater than stem.
Distance to −38° C. or −36° F. Line from Bottom of Bulb: 120 to 130 mm. (4.73 to 5.12 in.).
Distance to +49° C. or +120° F. Line from Top of Thermometer: 19 to 25 mm. (0.75 to 0.98 in.).
Expansion Chamber: To permit heating to 100° C. or 212° F.
Filling above Mercury: Nitrogen gas.
Top Finish: Plain.
Graduation: All lines, figures, and letters clear cut and distinct. Lines at multiples of 5° C. or 10° F. to be longer than the remaining lines. Graduations to be numbered at each multiple of 10° C. or 20° F.
Immersion: 108 mm. or 4¼ in. The words "108-mm. immersion" on Centigrade thermometers or "4¼-in. immersion" on Fahrenheit thermometers and a line around the stem 108.0 mm. or 4.25 in. above the bottom of the bulb shall be etched on the thermometer.
Special Marking: "A. S. T. M. Cloud and Pour," a serial number and the manufacturer's name or trade mark shall be etched on the stem.
Scale Error: The error at any point of the scale, when the thermometer is standardized as provided below, shall not exceed 0.5° C. or 1° F.
Standardization: The thermometer shall be standardized at the ice point and at intervals of approximately 20° C. or 40° F. for 108-mm. or 4¼-in. immersion and for an average temperature of 21° C. or 70° F. for the emergent mercury column.
Case: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. Cloud and Pour, −38 to +50° C." or "A. S. T. M. Cloud and Pour, −36 to +120° F." according to the type of thermometer.

Note.—For the purpose of interpreting these specifications the following definitions apply:
The total length is the over-all length of the finished instrument.
The diameter is that measured with a ring gage.
The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.
The top of the thermometer is the top of the finished instrument.

(*b*) These specifications cover a special low cloud and pour test thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −60° to +20° C. or −70° to +70° F.

Type: Etched stem, glass.
Liquid: Toluene or other suitable liquid colored red with a permanent dye.
Range and Subdivision: −60° to +20° C. in 1° C. or −70° to +70° F. in 2° F.
Total Length: 227 to 231 mm. (8.92 to 9.08 in.).
Stem: Plain front, enamel back, suitable thermometer tubing. Diameter 7.0 to 8.0 mm. (0.28 to 0.31 in.).
Bulb: Corning normal or equally suitable thermometric glass.
Length, 8.0 to 9.5 mm. (0.31 to 0.37 in.).
Diameter, 5.0 to 6.5 mm. (0.22 to 0.26 in.).
Distance to −57° C. or −70° F. Line from Bottom of Bulb: 120 to 130 mm. (4.73 to 5.12 in.).
Distance to +20° C. or +68° F. Line from Top of Thermometer: 35 to 45 mm. (1.38 to 1.77 in.).
Expansion Chamber: To permit heating to +60° C. or +140° F.
Filling above Liquid: Gas under pressure.
Top Finish: Plain.
Graduation: All lines, figures and letters clear cut and distinct, lines at multiples of 5° C. or 10° F. to be longer than the remaining lines. Graduations to be numbered at each multiple of 10° C. or 20° F.

IMMERSION: 108 mm. (4¼ in.). The words "108-mm. immersion" on Centigrade thermometers, or "4¼-in. immersion" on Fahrenheit thermometers and a line around the stem 108 mm. (4.25 in.) above the bottom of the bulb, shall be etched on the thermometer.

SPECIAL MARKING: "A. S. T. M. Low Cloud and Pour" a serial number and the manufacturer's name or trade mark shall be etched on the thermometer.

SCALE ERROR: The error at any point of the scale when the thermometer is standardized as provided below, shall not exceed 1° C. or 2° F.

STANDARDIZATION: The thermometer shall be standardized at the ice point and at intervals of approximately 20° C. or 35° F. for 108-mm. or 4¼-in. immersion, and for an average temperature of 21° C. or 70° F. for the emergent liquid column.

CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking "A. S. T. M. Low Cloud and Pour, −60° to +20° C." or "A. S. T. M. Low Cloud and Pour, −70° to +70° F.," according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications, the following definitions apply:

The total length is the overall length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

The cork, *c*, shall fit the test jar, and shall be bored centrally to take the test thermometer. The jacket, *d*, shall be of glass or metal, shall be water tight, of cylindrical form, flat bottom, about 4½ in. deep, with inside diameter ⅜ to ½ in. greater than outside diameter of the test jar.

A disk of cork or felt, *e*, ¼ in. thick and of the same diameter as the inside of the jacket will be required.

The ring gasket, *f*, shall be about $\frac{3}{16}$ in. thick, and made to fit snugly around the outside of the test jar and loosely inside the jacket. This gasket may be made of cork, felt or other suitable material, elastic enough to cling to the test jar and hard enough to hold its shape. The purpose of the ring gasket is to prevent the test jar from touching the jacket.

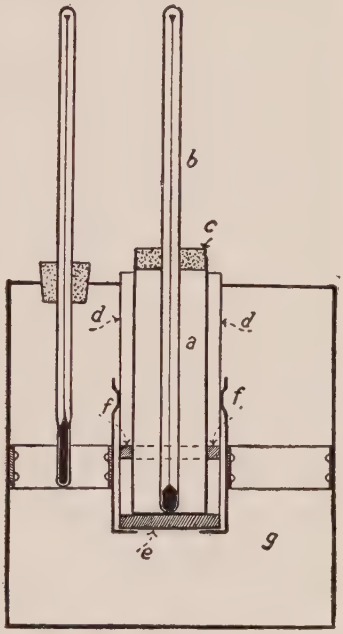


FIG. 246.—Apparatus for Cloud and Pour Test (as assembled for Cloud Test).

The cooling bath, *g*, shall be of a type suitable for obtaining the required temperatures. The size and shape of the bath are optional but a support, suitable for holding the jacket firmly in a vertical position, is essential. For determination of pour points below 50° F., two or more baths should be at hand. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable freezing mixtures.

NOTE.—The freezing mixtures commonly used are as follows:

For temperatures down to 50° F., ice and water.
" " " " 10° F., crushed ice and sodium chloride.
" " " " −15° F., crushed ice and calcium chloride crystals.
" " " " −70° F., solid carbon dioxide and acetone or gasoline.

The last named mixture may be made as follows: In a covered metal beaker chill a suitable amount of acetone or gasoline to 10° F., or lower, by means of an ice-salt mixture. Invert a cylinder of liquid carbon dioxide and draw off carefully into a chamois skin bag the desired amount of carbon dioxide, which through rapid evaporation will quickly become solid. Then add to the chilled acetone or gasoline enough of the solid carbon dioxide to give the desired temperature.

Procedure.—The oil to be tested shall be brought to a temperature at least 25° F. above the approximate cloud point. Moisture, if present, shall be removed by any suitable method, as by filtration through dry filter paper until the oil is perfectly clear, but such filtration shall be made at a temperature at least 25° F. above the approximate cloud point.

The clear oil shall be poured into the test jar, *a*, to a height of not less than 2 nor more than 2¼ in. The test jar may be marked to indicate the proper level.

The test jar shall be tightly closed by the cork, *c*, carrying the test thermometer, *b*, in a vertical position in the center of the jar with the thermometer bulb resting on the bottom of the jar.

The disk, *e*, shall be placed in the bottom of the jacket, *d*, and the test jar with the ring gasket, *f*, 1 in. above the bottom shall be inserted into the jacket The disk, jacket and inside of jacket shall be clean and dry.

The temperature of the cooling bath, *g*, shall be maintained at 30 to 35° F. The jacket, containing the test jar, shall be supported firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium.

At each test thermometer reading which is a multiple of 2° F., the test jar shall be removed from the jacket, quickly but without disturbing the oil, inspected for cloud, and replaced in the jacket. This complete operation shall require not more than three seconds. If the oil does not show a cloud when it has been cooled to 50° F., the test jar shall be placed in a second bath maintained at a temperature of 0° to +5° F. If the oil does not show a cloud when it has been cooled to 20° F., the test jar shall be placed in a third bath maintained at a temperature of −30° to −25° F.

When such inspection first reveals a distinct cloudiness or haze in the oil, at the bottom of the test jar, the reading of the test thermometer, corrected for error if necessary, shall be recorded as the cloud point.

Procedure for Pour Point.—The oil shall be poured into the test jar, *a*, to a height of not less than 2 nor more than 2¼ in. The jar may be marked to indicate the proper level. When necessary, the oil shall be heated in a water bath just sufficiently for pouring into the test jar.

The test jar shall be tightly closed by the cork, *c*, carrying the test thermometer, *b*, in a vertical position in the center of the jar with the thermometer bulb immersed so that the beginning of the capillary shall be ⅛ in. below the surface of the oil.

Heat without stirring to a temperature of 115° F. in a bath maintained at not higher than 118° F. The oil shall then be cooled to 90° F. in air or in a water bath approximately 77° F. in temperature. Oils on which a pour point below −30° F. is expected shall be heated as above with the high cloud- and pour-test thermometer in position, cooled to 60° F. and the low cloud- and pour-test thermometer placed in position and the assembly placed in the jacket. Oils

on which a pour point of above 90° F. is expected shall be heated to 115° F. or to a temperature 15° F. above the expected pour point, with the high cloud- and pour-test thermometer in position, and the test jar immediately introduced into the jacket.

The disk, *e*, shall be placed in the bottom of the jacket, *d*, and the test jar, with the ring gasket, *f*, 1 in. above the bottom, shall be inserted into the jacket. The disk, gasket and inside of jacket shall be clean and dry.

After the oil has cooled enough to allow the formation of paraffin wax crystals, great care shall be taken not to disturb the mass of the oil nor to permit the thermometer to shift in the oil. Any disturbance of the spongy network of wax crystals will lead to low and fictitious results.

The temperature of the cooling bath, *g*, shall be maintained at 30° to 35° F. The jacket, containing the test jar, shall be supported firmly in a vertical position in the cooling bath so that not more than 1 in. of the jacket projects out of the cooling medium.

Beginning at a temperature 20° F. before the expected pour point, at each test thermometer reading which is a multiple of 5° F., the test jar shall be removed from the jacket carefully and shall be tilted just enough to ascertain whether there is a movement of the oil in the test jar. The complete operation of removal and replacement shall require not more than 3 seconds. If the oil has not ceased to flow when its temperature has reached 50° F., the test jar shall be placed in the jacket in a second bath maintained at a temperature of 0° to +5° F. If the oil has not ceased to flow when its temperature has reached 20° F., the test jar shall be placed in the jacket in a third bath maintained at a temperature of −30° to −25° F. For determinations of very low pour points, additional baths should be maintained with successively lower temperature differentials of about 30° F. In each case the test jar shall be transferred when the temperature of the oil reaches a point 50° F. above the temperature of the new bath. At no time shall the cold test jar be placed directly in the cooling medium. As soon as the oil in the test jar does not flow when the jar is tilted, the test jar shall be held in a horizontal position for exactly 5 seconds, as noted by a stop watch or other accurate timing device and observed carefully. If the oil shows any movement under these conditions, the test jar shall be immediately replaced in the jacket and a test for flow repeated at the next temperature 5° F. lower.

The test shall be continued in this manner until a point is reached at which the oil in the test jar shows no movement when the test jar is held in a horizontal position for exactly five seconds. Certain lubricating oils tend to move as a whole and should be very closely observed. The reading of the test thermometer at this temperature, corrected for error if necessary, shall be recorded. The pour point shall be taken as the temperature 5° F. above this solid point.

Special Procedure for Black Oils and Cylinder Stocks.—(*a*) In those cases where it is known that a sample has been subjected to some temperature higher than 115° F. during the preceding 24 hours, or where the history of the sample in this respect is not known, the sample shall be held in the laboratory 24 hours before testing, unless three consecutive tests of the same sample in the same test jar give check results. For these particular oils, results obtained by one or the other of the alternative procedures shall be called the upper (maximum) pour point.

(*b*) The lower (minimum) pour point shall be determined by heating a sample with stirring to 220° F. The oil shall then be poured in the test jar, cooled to 90° F. as before, and the pour point determined as described in Section on "Procedure for Pour Point."

(*c*) The upper and lower pour points shall be reported separately.

STANDARD METHOD OF TEST FOR FLASH AND FIRE POINTS BY MEANS OF OPEN CUP [27]

A. S. T. M. Designation: D 92–33 [28]

Scope.—The open cup flash and fire test on all products except fuel oils and those having an open cup flash below 175° F. shall be determined in the Cleveland Open Cup.

Apparatus.—The Cleveland open cup, a diagram of which appears in Fig. 247, shall include the following major parts:

(*a*) ***Flash Cup.***—The cup shall be made of brass and shall conform to the following requirements:

	Inches			Centimeters		
	Min.	Normal	Max.	Min.	Normal	Max.
Inside diameter immediately below filling mark	$2\frac{15}{32}$	$2\frac{1}{2}$	$2\frac{17}{32}$	6.27	6.35	6.43
Outside diameter below flange	$2\frac{21}{32}$	$2\frac{11}{16}$	$2\frac{23}{32}$	6.75	6.83	6.91
Inside height from center of bottom to rim	$1\frac{9}{32}$	$1\frac{5}{16}$	$1\frac{11}{32}$	3.25	3.33	3.41
Thickness of bottom	$\frac{7}{64}$	$\frac{1}{8}$	$\frac{9}{64}$	0.28	0.32	0.36
Distance from rim to filling mark	$\frac{23}{64}$	$\frac{3}{8}$	$\frac{25}{64}$	0.91	0.95	0.99
Distance lower surface flange to bottom of cup	$1\frac{7}{32}$	$1\frac{1}{4}$	$1\frac{9}{32}$	3.10	3.18	3.26
Vertical distance upper surface flange to rim	$\frac{7}{64}$	$\frac{1}{8}$	$\frac{9}{64}$	0.28	0.32	0.36
Thickness of rim	$\frac{5}{64}$	$\frac{3}{32}$	$\frac{7}{64}$	0.20	0.24	0.28
Width of lower surface of flange	$\frac{9}{16}$	$\frac{19}{32}$	$\frac{5}{8}$	1.43	1.51	1.59

The bevelled edge of the cup shall be at an angle of approximately 45°. There may be a fillet of approximately $\frac{5}{32}$ in. (0.397 cm.) radius inside the bottom of the cup.

(*b*) ***Heating Plate.***—The cup shall be supported by a metal plate $\frac{1}{4}$ in. (0.635 cm.) in thickness and 6 in. (15.24 cm.) in width. The plate shall be of brass, cast iron, wrought iron or steel. In the center of the plate there shall be a plane depression $\frac{1}{32}$ in. (0.079 cm.) in depth, and of just sufficient diameter to fit the cup. There shall be a circular opening $2\frac{3}{16}$ in. (5.50 cm.) in diameter,

[27] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[28] This method is issued under the fixed designation D 92; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1921; Adopted in Amended Form, 1924; Revised, 1933 This method has been approved as American Standard by the American Standards Association.

cut through the plate, centering with the center of the above-mentioned depression. The plate shall be covered with a sheet of hard asbestos board ¼ in. in thickness, and of the same shape as the metal plate. There shall be cut in the

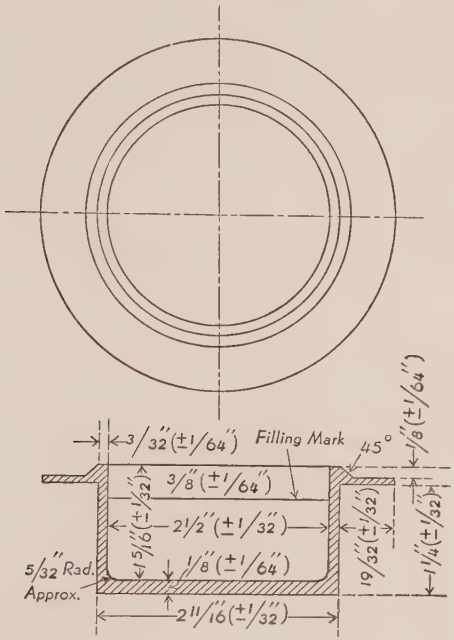


Fig. 247.—Cleveland Open Cup.

center of the asbestos board a circular hole just fitting the cup. Heat may be supplied from any convenient source. The use of a gas burner, electric heater, or alcohol lamp is permitted, but under no circumstances are products of combustion or free flame allowed to come up around the cup. The source of heat shall be centered under the opening in the plate and shall be of a type that will not produce local superheating. If a flame heater is used, it may be protected from drafts or excessive radiation by any suitable type of shield, that does not project above the level of the upper surface of the asbestos board.

Thermometer.—The thermometer shall conform to the following requirements. These specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −6° to +400° C., or +20° to +760° F., respectively.

Type: Etched stem, glass.
Liquid: Mercury.
Range and Subdivision: −6° to +400° C. in 2° C. or +20° to +760° F. in 5° F.
Total Length: 303 to 307 mm. (11.92 to 12.08 in.).
Stem: Plain front, enamel back, suitable thermometer tubing.
Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).
Bulb: Corning normal or equally suitable thermometric glass.
Length, not over 13 mm. (0.51 in.).
Diameter, not greater than stem.

Distance to −6° C. or 20° F. Line from Bottom of Bulb: 40 to 50 mm. (1.57 to 1.97 in.).

Distance to 400° C. or 760° F. Line from Top of Thermometer: 30 to 45 mm. (1.18 to 1.77 in.).

Filling above Mercury: Nitrogen gas.

Top Finish: Red glass ring.

Graduation: All lines, figures, and letters clear cut and distinct. The 10° C. lines or the first and each succeeding 10° F. line to be longer than the intermediate lines. Graduations to be numbered at each multiple of 10° C. or 20° F.

Immersion: 25 mm. or 1 in. The words "25 mm. immersion" on Centigrade thermometers or "1-in. immersion" on Fahrenheit thermometers and a line around the stem 25.4 mm. or 1.00 in. above the bottom of the bulb shall be etched on the thermometer.

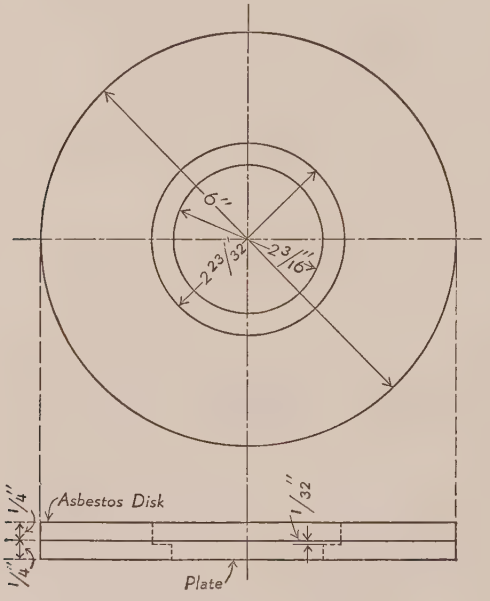


Fig. 248.—Heating Plate.

Special Marking: "A. S. T. M. Open Flash" a serial number and the manufacturer's name or trade mark shall be etched on the stem.

Scale Error: The error at any point of the scale when the thermometer is standardized as provided below shall not exceed 1° C. up to 372° C. or 2½° F. up to 700° F.

Standardization: The thermometer shall be standardized at the ice point and at intervals of approximately 100° F. for 25-mm. or 1-in. immersion and for the following temperatures of the emergent mercury column:

Thermometer Reading		Average Temperature of Emergent Mercury Column	
100° C.	200° F.	44° C.	110° F.
150° C.	300° F.	54° C.	129° F.
200° C.	400° F.	64° C.	150° F.
250° C.	500° F.	77° C.	175° F.
300° C.	600° F.	91° C.	205° F.
350° C.	700° F.	108° C.	240° F.

TEST FOR PERMANENCY OF RANGE: After being subjected to a temperature between 360 to 370° C. or 680 to 700° F. for 24 hours, the accuracy shall be within the limit specified.

CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. Open Flash, −6° to +400° C." or "A. S. T. M. Open Flash, +20° to +760° F.," according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

Procedure.—(*a*) The thermometer shall be suspended or held in a vertical position by any suitable device. The bottom of the bulb shall be ¼ in. (0.635 cm.) [29] from the bottom of the cup, and above a point half way between the center and back of the cup.

(*b*) The cup shall be filled with the oil to be tested in such a manner that the top of the meniscus is exactly at the filling line at room temperature. When asphalt or other solid bituminous material is to be tested, it shall first be heated to a temperature not less than 300° F. nor more than 350° F., to render it sufficiently fluid. The cup shall then be filled with the hot fluid at this temperature in the same manner as with oil. The subsequent procedure shall then be the same for both asphalt and solid bituminous material as with oil. The surface of the oil shall be free from bubbles. There shall be no oil above the filling line or on the outside of the apparatus.

(*c*) The test flame shall be approximately $\frac{5}{32}$ in. (0.397 cm.) in diameter.

NOTE.—For purposes of comparison it is recommended that a bead of suitable light colored material be mounted in a convenient position so that the size of the test flame can be determined. The device for applying the flame may be of any suitable type but it is suggested that the tip be approximately $\frac{1}{16}$ in. (0.159 cm.) in diameter at the end and that the orifice be $\frac{1}{32}$ in. (0.079 cm.) in diameter. If the device for operating the test flame be mounted in such a manner as to permit automatic duplication of the sweep of the test flame the radius of swing shall be not less than 6 in.

(*d*) The test flame shall be applied as the temperature read on the thermometer reaches each successive 5° F. mark. The flame shall pass in a straight line (or on the circumference of a circle having a radius of at least 6 in.) across the center of the cup and at right angles to the diameter passing through the thermometer. The test flame shall, while passing across the surface of the oil, be in the plane of the upper edge of the cup. The time for the passage of the test flame across the cup shall be approximately one second.

(*e*) The oil shall be heated at a rate not exceeding 30° F. per minute temperature rise, till a point is reached approximately 100° F. below the probable flash point of the oil. Thereafter the rate of heating shall be decreased and for at least the last 50° F. before the flash point is reached, the rate shall be not less than 9 nor more than 11° F. per minute.

The flash point shall be taken as the temperature read on the thermometer when a flash appears at any point on the surface of the oil. The true flash must not be confused with a bluish halo that sometimes surrounds the test flame.

[29] The immersion line engraved on the thermometer stem will be $\frac{1}{16}$ in. (0.159 cm.) below the level of the rim of the cup.

After determining the flash point, the heating shall be continued at the specified rate of 9 to 11° F. per minute, and application of the test flame shall be made at the specified intervals until the oil ignites and continues to burn for a period of at least 5 seconds. The method of application of the flame shall be the same as for flash point. The temperature read at the time of the flame application which causes burning for a period of 5 seconds or more shall be recorded as the fire point.

Precautions.—The flash point and fire point tests shall be made in a room or compartment free from air drafts. The operator shall avoid breathing over the surface of the oil. It is desirable that the room or compartment be darkened sufficiently so that the flash may be readily discernible.

Detection of Soap.—To increase the viscosity of an oil,[30] resort is had to the use of "oil pulp," "oil-thickener," or "white gelatin," usually an oleate of aluminum, though other bases may be present. Its disadvantages are that it causes the oil to chill more easily and to emulsify, thus increasing the friction. Furthermore, it is precipitated by contact with water or steam, causing clogging of the machinery.

The test depends upon the fact that the metaphosphates of the earthy and alkali metals and aluminum are insoluble in absolute alcohol.[31]

The test is applied as follows: five to 10 ml. of the oil to be tested are dissolved in about 5 ml. of 86° gasoline or ether, and about 15 drops of the phosphoric acid solution (Reagents, p. 1799) added, shaken and allowed to stand; the formation of a flocculent precipitate indicates the presence of soap. An idea of the kind of soap can be often gained by adding an alcoholic solution of $PtCl_4$. If the precipitate becomes crystalline, it is a potash soap; if it dissolves, soda, lime, or magnesia; if unchanged, alumina or iron.

For the accurate determination of these compounds a known weight of the oil must be ignited, the residue determined and quantitatively examined.

Caoutchouc.—Holde [32] states that 1 to 2% of unvulcanized caoutchouc is sometimes added to oils to increase their viscosity. This may be detected by adding three parts of alcohol to four parts of the ethereal solution, whereby the rubber material is precipitated and may be dried and weighed.

Test for Fatty Oils.—To detect small quantities of fatty oil (¼ to 2%) Lux [33] recommends heating a few ml. of the oil for fifteen minutes with some bits of sodium in a test-tube in an oil bath; a similar test is made with sodium hydroxide. The temperature employed should be for light oils about 230°, for dark oils 250°.[34] In case fatty oil be present, the contents of one or both of the tubes solidify to a jelly of greater or less consistence according to the amount of fatty oil present.

The quantitative determination of these oils, as for example in cylinder oils, is effected after the manner of determining the saponification value (p. 1771) or the detection of unsaponifiable oils in fatty oils (page 1773).

[30] In a case which came to the writer's notice the oil would not flow out of the Saybolt "A" apparatus at 70°, at 85° required 1167″, and at 110°, 181″.

[31] Schweitzer and Lungwitz, J. Soc. Chem. Ind., **13**, 1178, 1894.

[32] "Examination of Hydrocarbon Oils," p. 202.

[33] Z. anal. Chem., **24**, 357, 1885.

[34] Holde, Examination of Hydrocarbon Oils, p. 76.

Schreiber [35] adopts a method similar to Sweetham and Henriques, in that he dissolves 5 grams of the oil in 25 ml. of benzol, adds 25–50 ml. N/2 alcoholic potash, and boils for half an hour on the water bath, using a 3-ft. glass tube as a condenser.

Gumming Test.[36]—This is designed to give an idea of the amount of a change that may be expected in a mineral oil when in use. These resinified products increase the friction of the revolving or rubbing surfaces.[37] It is also a measure of the amount that an oil will " carbonize " in a gas or gasoline engine cylinder. It is applied after the manner of the elaidin test, by thoroughly mixing together 5 grams of the oil in a cordial glass with 11 grams of nitrosulfuric acid and cooling by immersion in a pan of water at 10–15°. Brownish spots or, in case of a bad oil, masses, form around the edges and become red in the course of two hours.

As shown by long practical experience, the oil showing the least tar or gum is the best oil; it also absorbs the least oxygen.

STANDARD METHOD OF TEST FOR CARBON RESIDUE OF PETROLEUM PRODUCTS [38]

(CONRADSON CARBON RESIDUE)

A. S. T. M. Designation: D 189–36 [39]

Scope.—This method of test is a means of determining the amount of carbon residue left on evaporating an oil under specified conditions, and is intended to throw some light on the relative carbon-forming propensity of an oil. The results of the test must be considered in connection with other tests and the use for which the oil is intended. This test furnishes pertinent information relative to lubricants for internal combustion engines, domestic oil fuels, and oils used in the manufacture of gas.

Apparatus.—The apparatus (see Fig. 249) shall consist of the following:

(*a*) Porcelain crucible, wide form, glazed throughout, or a silica crucible; 29 to 31-ml. capacity, 46 to 49 mm. (1.81 to 1.93 in.) in rim diameter.

(*b*) Skidmore iron crucible flanged and ringed, 65 to 82-ml. capacity, 53 to 57 mm. (2.07 to 2.20 in.) inside and 60 to 67 mm. (2.36 to 2.64 in.) outside

[35] J. Am. Chem. Soc., **29**, 74, 1907.

[36] Gill, J. Am. Chem. Soc., **24**, 467, 1902.

[37] Aisinman, J. Soc. Chem. Ind., **14**, 282, 1895.

[38] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

This procedure is a modification of the original Conradson method and apparatus for Carbon Test and Ash Residue in Petroleum Lubricating Oils. See Proceedings, Eighth International Congress of Applied Chemistry, New York, September, 1912, Vol. I, p. 131; also Journal of Industrial and Engineering Chemistry, Vol. 4, No. 11, December, 1912.

[39] This method is issued under the fixed designation D 189; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1924; Adopted in Amended Form, 1928; Revised, 1930, 1936.

diameter of flange, 37 to 39 mm. (1.46 to 1.54 in.) in height supplied with a cover without delivery tubes and having the vertical opening closed. The horizontal opening of about 6.5 mm. (0.26 in.) shall be kept clean. The outside diameter of the flat bottom shall be 30 to 32 mm. (1.18 to 1.26 in.).

(*c*) Spun sheet-iron crucible, with cover; 78 to 82 mm. (3.07 to 3.23 in.) in outside diameter at the top, 58 to 60 mm. (approximately 2.3 in.) in height, and approximately 0.8 mm. (0.03 in.) in thickness. Place at the bottom of this crucible, and level before each test, a layer of about 25 ml. of dry sand, or enough to bring the Skidmore crucible, with cover on, nearly to the top of the sheet-iron crucible.

(*d*) Triangle of bare nichrome wire of approximately No. 13 B. & S. gage having an opening small enough to support the bottom of the sheet-iron crucible at the same level as the bottom of the asbestos block or hollow sheet-metal box, Paragraph (*f*).

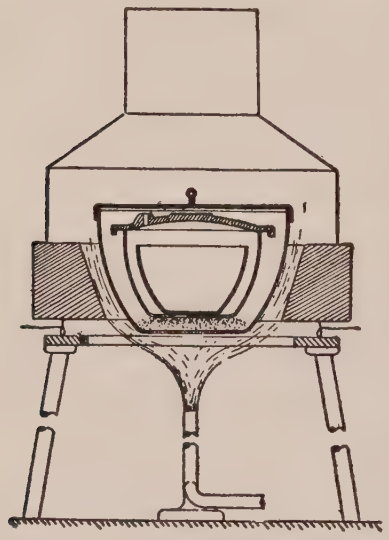


Fig. 249.—Apparatus for Determining Carbon Residue.

(*e*) Circular sheet-iron hood from 120 to 130 mm. (4¾ to 5¼ in.) in diameter the height of the lower perpendicular side to be from 50 to 53 mm. (2 to 2⅛ in.); provided at the top with a chimney 50 to 60 mm. (2 to 2½ in.) in height and from 50 to 56 mm. (2 to 2¼ in.) inside diameter, which is attached to the lower part having the perpendicular sides by a cone-shaped member, bringing the total height of the complete hood from 125 to 130 mm. (5⅛ in.). The hood may be made from a single piece of metal provided the foregoing dimensions are adhered to. As a guide for the height of the flame above the chimney, a bridge made of approximately 3-mm. (⅛-in.) iron or nichrome wire, h, shall be attached having a height of 50 mm. (2 in.) above the top of the chimney.

(*f*) Asbestos, block refractory ring, or hollow sheet-metal box, 150 to 175 mm. (6 to 7 in.) in diameter if round or on a side if square, 32 to 38 mm. (1¼ to 1½ in.) in thickness, provided with a metal-lined, inverted cone-shaped opening through the center; 83 mm. (3¼ in.) in diameter at the bottom, and 89 mm. (3½ in.) in diameter at the top.

(*g*) Burner, Meker type, 24 mm. (1 in.) in diameter by 155 mm. (6 in.) in height, suitable for either manufactured or natural gas.

Procedure.—The test shall be conducted as follows:

Place two glass beads about 0.1 in. in diameter in, and include them in the weight of, the tared porcelain or silica crucible in which is accurately weighed 10 g. of the oil to be tested, free from moisture or other suspended matter. Place this crucible in the center of the Skidmore crucible. Level the sand in the large sheet-iron crucible and set the Skidmore crucible on it in the exact

center of the iron crucible. Apply covers to both the Skidmore and the iron crucible, the one to the latter fitting loosely to allow free exit to the vapors as formed.

On a suitable stand or ring, place the bare nichrome wire triangle and on it the asbestos block or hollow sheet-metal box. Next, centre the sheet-iron crucible in the block with its bottom resting on top of the triangle, and cover the whole with the sheet-iron hood in order to distribute the heat uniformly during the process (see Fig. 249).

Apply heat with a high strong flame from the Meker-type gas burner, so that the pre-ignition period will be 10 minutes $\pm 1\frac{1}{2}$ minutes (a shorter time may start the distillation so rapidly as to cause foaming or too high a flame). When smoke appears above the chimney, immediately move or tilt the burner so that the gas flame plays on the sides of the crucible for the purpose of igniting vapors. Then remove the heat temporarily, and before replacing adjust by screwing down the pinch-cock on the gas tubing so that the ignited vapors burn uniformly with the flame above the chimney but not above the wire bridge. Heat may be increased, if necessary, when the flame does not show above the chimney. The period of burning the vapors shall be 13 minutes ± 1 minute.

When the vapors cease to burn and no further blue smoke can be observed, readjust the burner and hold the heat as at the beginning so as to make the bottom and lower part of the sheet-iron crucible a cherry red and maintain for exactly 7 minutes. The total period of heating shall be 30 minutes ± 2 minutes which constitutes an additional limitation on the tolerances for the pre-ignition and burning periods. There should be no difficulty in carrying out the test exactly as directed with the gas burner of the type named, using city gas (about 550 B.t.u.) with the top of the burner about 2 in. below the bottom of the crucible. The time periods shall be observed with whatever burner and gas is used.

Remove the burner and allow the apparatus to cool until no smoke appears, and then remove the cover of the Skidmore crucible (about 15 minutes). Remove the porcelain or silica crucible with heated tongs, place in the desiccator, cool and weigh. Calculate the percentage of carbon residue on the original sample.

Special Procedure: *Special Procedure for Oils Having Carbon Residues in Excess of 5%, Such as Heavy Crude Oils, Residuums, Heavy Fuel Oils, and Heavy Gas-Enrichment Oils.*—When the carbon residue as obtained by the procedure described above (using a 10-g. sample) is in excess of 5%, difficulties may be experienced due to boiling over of the sample. Trouble also may be encountered with samples of heavy products which are difficult to dehydrate. In the case, therefore, of samples showing by the usual method of test a carbon residue in excess of 5%, the test shall be repeated in duplicate using a 5-g. sample.

Tolerances.—Weights of oil sample shall be accurate to within 5 mg. Tests shall be run in duplicate and repeated if necessary until the percentages of carbon residue differ by not more than 10% from an average.

Gasoline Test.—This shows the presence of tar (still bottoms) or asphaltic matters.

Mix 10 ml. of the oil with 90 ml. 86°–88° gasoline (from Pennsylvania crude) B. pt. 30°–50° C., allow to stand one hour at 70° to 80° F.; not more than 10% of flocculent or tarry matter should have settled out. This settling can be facilitated by whirling in a centrifuge in a graduated tube in which the volume of the precipitate can be read off. If the test be applied to the oil before making the flash test and then again after this test it shows the extent to which the oil is changed upon heating. Other things being equal the oil which is changed the least is the best oil. See page 1761.

Microscopical Test.—Put a few drops of the well-mixed oil on a slide and note the nature of the suspended matter—whether carbonaceous specks, flakes of paraffin which disappear on warming, or foreign matter. A good oil should be practically free from all these bodies.

Heat Test.—Heat 20–25 ml. of the oil in an Erlenmeyer flask or beaker, nearly to the flashing point and keep it at this temperature for fifteen minutes; a satisfactory oil will darken, but remain clear even after standing a day. A poorly refined oil changes to jet black, and forms a carbon-like precipitate. This is usually indicative of an oil that has been refined by acid treatment.

Herschel's Demulsibility Test.[40] ***Method 320.31.***—The test is applicable to non-emulsifying oils, such as are used with high speed engines and turbines, and in its present form does not apply to steam cylinder or other compounded oils. It is made as follows:

Twenty ml. of oil and 40 ml. of distilled water are placed in a 100 ml. cylinder having an inside diameter of 2.6 cm. and heated to 55°. The oil and water are then mixed or emulsified by stirring with a paddle for five minutes at a speed of 1500 R.P.M. The paddle is simply a metal plate 89 by 20 by 1.5 mm. thick, conveniently driven by an electric motor.

The rate at which the oil settles out from the emulsion, when it is allowed to stand at a temperature of 55° C. is a measure of the emulsibility of the oil. There is a tendency for the rate of settling out of the oil to increase up to a maximum and then decrease, and we may take readings every five minutes (or every minute if the oil separates out rapidly) and note the maximum rate. For example, the following readings were obtained for a certain oil:

Time	Time Since Stopping Paddle	Reading of Cylinder at Top of Emulsion	Ml. of Oil Settled Out	Rate of Settling Ml. per Hour
9.50.....	0	60	0	0
9.55.....	5	57	3	36
10.02.....	12	47	13	65
10.05.....	15	43	19	68
10.10.....	20	41	17	57

The maximum rate is here 68 ml. per hour, and this is called the "demulsibility." The best transformer, motor, and turbine oils settle out in one minute or less, so that if we take readings to even minutes and even ml., the rate would be 1200. Oils are found with rates all the way down from this maximum rate to zero.

[40] Bur. Mines Bull. 323B.

It has been found necessary to shake the container holding the sample of oil if it has been allowed to stand for some time, or otherwise the oil poured off from the top may show a different rate of settling from the oil at the bottom. It is also necessary to protect the oil from sunlight which has the effect of decreasing the rate of settling.

With some oils, under certain conditions, part of the water does not enter into the emulsion and drops of oil adhere to the sides of the cylinder. When this phenomenon occurs, the rate of settling, indicated by the test, is apt to be incorrectly high. The adhering drops may be avoided by using a lower speed or less water, the total quantity of oil and water being kept equal to 60 ml. If part of the water does not enter into the emulsion, but we do not have the above described phenomenon, complete emulsification may sometimes be obtained by prolonging the stirring beyond five minutes, or by increasing the speed.

Friction Tests.—The writer doubts if friction tests are worth the outlay for a machine and the time expended in their execution. Without question they do determine the relative efficiency as regards lubricating power of different oils, but the conditions under which the test is made seldom occur in practice; the bearings upon which the oil is tested are as nearly perfect as can be made, and the feed and load are as regular as is possible; in other words, the conditions are ideal.

The lubricating power of an oil is so closely related to its viscosity [41] that the author believes that results of more practical value can be obtained by the determination of the viscosity of the oils, and subsequent observation of their behavior in actual use than by the longer and more troublesome friction test. Recent experiments,[42] however, have shown that of two oils of the same viscosity and other constants the coefficient of friction of one was 14% less than the other.

In case, however, it be desired to make the friction test, the following machines, it is believed, will be found to be most satisfactory for the purpose:

For spindle oils and light lubricating oils, the machine [43] of the Thurston type which can be run at the highest speed and lowest pressure.

For heavy oils and railroad work, the large machine of the Thurston [44] type, described also in Redwood Treatise on Petroleum, III, 851 (1922); also in Archbutt and Deeley.[45]

Color.—This is determined with the Union Colorimeter which uses standard glass plates, A. S. T. M. D 155–34 T.

[41] Brannt, "Petroleum and its Products," p. 510; Woodbury, *vide infra.*
[42] Trans. Am. Soc. Mech. Eng., **32**, 834, 1910.
[43] Made by Olsen or Riehlé Bros., Philadelphia, Pa.
[44] "Lubrication and Lubricants," 1907, pp. 332–348.
[45] Ibid., pp. 355, 359.

LIQUID FUELS

(*a*) *Gasoline.* The tests usually made are color,[46] doctor test,[46] corrosion, distillation, acidity, and sulfur.

The color, acidity, and sulfur tests are made as with kerosene.

The doctor test (sodium plumbite) is made as follows:[47]

Doctor Test (Sodium Plumbite)

Preparation of Reagents: (*1*) ***Sodium plumbite*** (***doctor solution***).—Dissolve approximately 125 grams of sodium hydroxide (NaOH) in 1 liter of distilled water. Add 60 grams of litharge (PbO) and shake vigorously for 15 minutes or let stand with occasional shaking for at least a day. Allow to settle and decant or siphon off the clear liquid. Filtration through a mat of asbestos may be employed if the solution does not settle clear. The solution should be kept in a tightly corked bottle and should be refiltered before use if not perfectly clear.

(*2*) ***Sulfur.***—Pure, dry flowers of sulfur.

Making of Test.—Shake vigorously together in a test tube 10 ml. of the sample to be tested and 5 ml. of sodium plumbite solution for about 15 seconds. Add a small pinch of flowers of sulfur, again shake for 15 seconds, and allow to settle. The quantity of sulfur used should be such that practically all of it floats on the interface between the sample and the sodium-plumbite solution.

Interpretation of Results.—If the sample is discolored, or if the yellow color of the sulfur film is noticeably masked, the test shall be reported as *positive* and the sample condemned as "sour." If the sample remains unchanged in color, and if the sulfur film is bright yellow or only slightly discolored with gray or flecked with black, the test shall be reported *negative* and the sample considered "sweet."

Corrosion Test (Copper Dish)

Apparatus.—A freshly polished hemispherical dish of spun copper ap-approximately 3½ inches in diameter.

Making of Test.—Place 100 ml. of the gasoline to be examined in the dish and place the dish in an opening of an actively boiling steam bath, so that the steam comes in contact with the outer surface of the dish up to the level of the gasoline. Leave the dish on the steam bath until all volatile material has disappeared.

Interpretation of the Results.—If the gasoline contains dissolved elementary sulfur or corrosive sulfur compounds, the bottom of the dish will be colored gray or black.

If the gasoline contains undesirable gum-forming constituents, there will be a weighable amount of gum deposited on the dish. Acid residues will show as gum in this test.

[46] Egloff says these tests will not long be required on account of expense and also that in the refining valuable anti-knock compounds are removed.

[47] Tech. Paper 323B.

STANDARD METHOD OF TEST FOR DETECTION OF FREE SULFUR AND CORROSIVE SULFUR COMPOUNDS IN GASOLINE [48]

A. S. T. M. Designation: D 130–30 [49]

This method of test shall be used for the detection of free sulfur and corrosive sulfur compounds in gasoline.

Procedure.—A clean strip of mechanically polished pure sheet copper about ½ in. in width and 3 in. in length shall be placed in a suitable clean tube or sample bottle. Gasoline under test shall be added so that the copper strip is completely immersed. The test tube or sample bottle shall be closed with a loosely fitting cork and held in a suitable bath at 122° F. (50° C.).

At the end of three hours the gasoline exposed strip shall be removed and shall be compared with a similar strip of freshly polished copper.

Detection of Sulfur.—The presence of sulfur or corrosive sulfur compounds is indicated by the corrosion or discoloration of the gasoline exposed strip when compared with the fresh copper strip.

(*a*) Gasoline shall be reported as passing the test when on examination the exposed strip shows not more than extremely slight discoloration as compared with the fresh copper strip.

(*b*) Gasoline shall be reported as not passing the test when on examination the exposed strip shows more than extremely slight discoloration as compared with the fresh copper strip.

Distillation of Gasoline

Apparatus and Procedure.—The apparatus and procedure have been given in method D 86–35, p. 1705:

Significance of Test.—R. E. Wilson [50] says, the 10% point is the best indication of ease of starting, vapor lock (that is stopping of engine by too volatile gasoline), and evaporation loss. The 50% point is important for good acceleration. The 90% point is related to the dew point and controls crank case dilution.

Octane Number is the per cent by volume of iso octane in a mixture of iso octane and normal heptane required to match the antiknock value of a given fuel.

[48] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[49] This method is issued under the fixed designation D 130; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1922; Adopted in Amended Form, 1930. This method has been approved as American Standard by the American Standards Association.

[50] Chem. Abs. **27**, 184.

FUEL OILS

The tests usually made are flash, viscosity, sulfur, water and sediment.

STANDARD METHOD OF TEST FOR FLASH POINT BY MEANS OF THE PENSKY–MARTENS CLOSED TESTER [51]

A. S. T. M. Designation: D 93–36 [52]

The A. S. T. M. standard Pensky-Martens closed tester shall be used for determining the flash point of fuel oil unless the use of the Tag closed tester is specified. In addition, a modified form of this method as described subsequently is used for the determination of the flash point of cut-back asphalts and other viscous materials and suspensions of solids.

Apparatus.—The A. S. T. M. Pensky-Martens tester, a diagram of which appears in Fig. 250, shall include the following major parts:

(*a*) ***Cup.***—The cup shall be made of brass and shall satisfy the following dimensional specifications:

Dimensions	Inches			Centimeters		
	Minimum	Normal	Maximum	Minimum	Normal	Maximum
Inside diameter below filling mark	1.950	2.000	2.050	4.953	5.080	5.207
Difference, inside and outside diameters below filling mark	0.120	0.125	0.130	0.305	0.318	0.330
Inside height	2.150	2.200	2.250	5.461	5.588	5.715
Thickness of bottom	0.070	0.095	0.120	0.178	0.241	0.305
Distance from rim to filling mark	0.845	0.860	0.875	2.146	2.184	2.223
Distance lower surface flange to bottom of cup	1.780	1.795	1.810	4.521	4.559	4.597

The inside of the cup may be turned to a slightly larger diameter above the filling mark and the outside may be tapered above the flange but the wall thickness at the upper edge shall be not less than 0.04 in. (0.102 cm.). The flange should be approximately 0.5 in. (1.27 cm.) wide and approximately 0.125 in. (0.318 cm.) thick. It shall be equipped with devices for locating the position of the lid on the cup and the cup in the stove. A handle, attached permanently to the flange of the cup, is a desirable accessory.

[51] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[52] This method is issued under the fixed designation D 93; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1921; Adopted in Amended Form, 1922; Revised, 1936. This method has been approved as American Standard by the American Standards Association.

(*b*) *Lid.*—

(*1*) *Stirring Device.*—The lid shall be equipped with a stirring device consisting of a vertical steel shaft, not less than 0.1 in. (0.254 cm.) nor more than 0.125 in. (0.318 cm.) in diameter, mounted in the center of the cup, and carrying two two-bladed brass propellers. The blades of both propellers shall be approximately 0.313 in. (0.795 cm.) wide and shall be set at an angle of

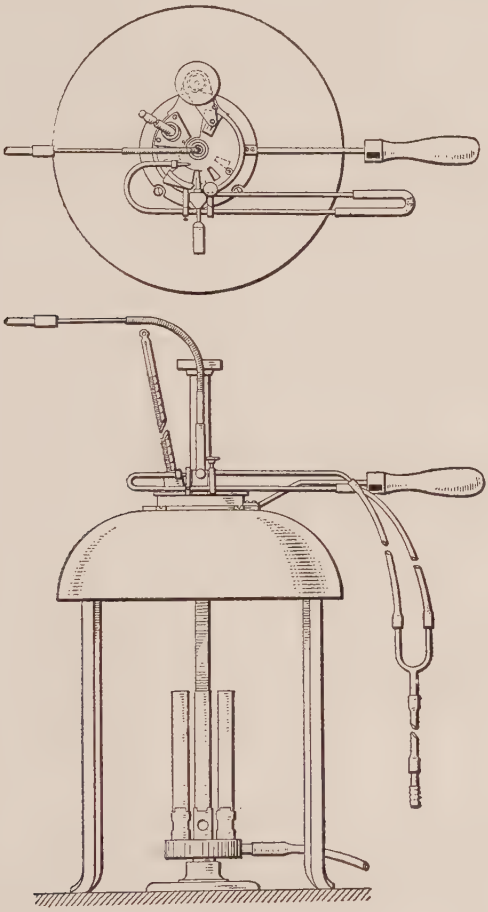


Fig. 250.—A. S. T. M. Standard Pensky-Martens Tester.

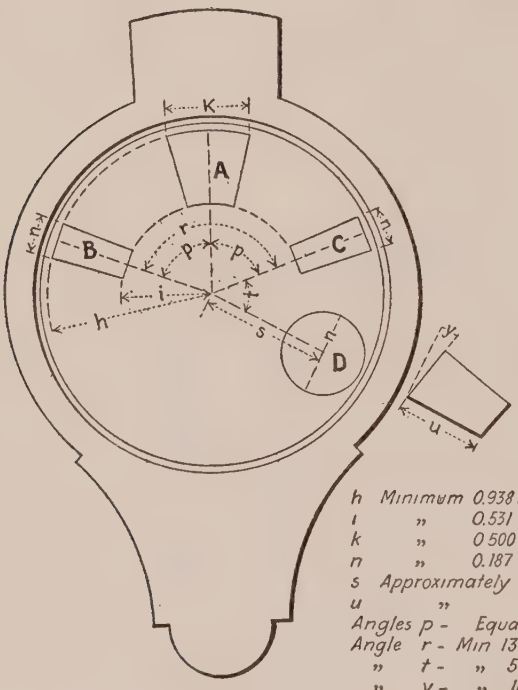
approximately 45°. The smaller (upper) propeller shall have an over-all diameter of approximately 0.75 in. (1.905 cm.). The larger (lower) propeller shall have an over-all diameter between 1.25 and 1.75 in. (3.175 and 4.445 cm.). The thickness of the propeller blades shall be not less than 0.057 in. (0.145 cm.) nor more than 0.081 in. (0.206 cm.), which limits correspond respectively to

No. 15 and No. 12 B. and S. gage sheet brass. The collars on which the propeller blades are mounted shall have horizontal and vertical dimensions not greater than 0.4 in. (1.016 cm.).

The plane of the center of the upper propeller shall be 0.4 in. (1.016 cm.) below the level of the rim of the cup. The plane of the center of the lower propeller shall be 2.0 in. (5.08 cm.) below the level of the rim of the cup. The level of the rim of the cup is in effect the level of the plane part of the portion of the lower surface of the lid inside the rim.

(*2*) ***Cover proper.***—The cover proper shall be of brass and shall have a rim projecting downward almost to the flange of the cup and fitting the outside of the cup closely. The thickness of the cover, measured just inside the rim shall be not less than 0.031 in. (0.079 cm.) nor more than 0.078 in. (0.198 cm.). There shall be a proper locating device engaging with a corresponding locating device on the flange of the cup.

There shall be four openings in the cover, as indicated in Fig. 251.



h	*Minimum*	*0.938 in.,*	*Maximum 0.969 in.*
i	"	*0.531* " ,	" *0.563* "
k	"	*0.500* " ,	" *0.540* "
n	"	*0.187* " ,	" *0.219* "
s	*Approximately*	*0.75 in.*	
u	"	*0.5* " .	
Angles p -	*Equal*		
Angle r -	*Min 135°;*	*Max. 140°.*	
" *t* -	" *50°,*	" *60°*	
" *y* -	" *10°,*	" *15°*	

Fig. 251.—Cover for A. S. T. M. Standard Pensky-Martens Tester.

Opening *A* is an area defined by arcs of two concentric circles and the intersected lengths of two radii. The radius of the outer circle shall be not less than 0.938 in. (2.383 cm.) nor more than 0.969 in. (2.461 cm.). The radius of the inner circle shall be not less than 0.531 in. (1.349 cm.) nor more than 0.563 in.

(1.430 cm.). The chord of the arc of the outer circle shall be not less than 0.500 in. (1.270 cm.) nor more than 0.540 in. (1.372 cm.).

Openings *B* and *C* are equal areas, each of the same general form as opening *A* but of approximately half the (angular) width. The radii of the defining inner and outer circles shall be within the limits specified for the radii of the two circles, arcs of which partly define opening *A*. The chord of the outer arc for opening *B* or opening *C* shall be not less than 0.187 in. (0.475 cm.) nor more than 0.219 in. (0.556 cm.). The sum of the areas of openings *B* and *C* shall be not less than 75% nor more than 100% of the area of opening *A*. Openings *B* and *C* shall be equally distant from opening *A* and radii drawn through each of their centers shall be at an angle of not less than 135° nor more than 140°.

Openings *A*, *B*, and *C* need not conform exactly to the shape of geometrical figures bounded by arcs of two concentric circles and intersected lengths of radii. Their boundaries must, however, fall on or between the lines indicated by the limiting values of the dimensional specification of the preceding text and of Fig. 251.

Opening *D* is for a thermometer collar. Its center is approximately 0.75 in. (1.905 cm.) from the center of the lid and on a radius at an angle of not less than 50° nor more than 60° from a radius passing through the center of opening *C*. The thermometer collar shall have an inside diameter of approximately 0.5 in. (1.27 cm.). It shall be set at an angle of not less than 10° nor more than 15° from the perpendicular.

(*3*) ***Shutter.***—The lid shall be equipped with a brass shutter, approximately 0.094 in. (0.239 cm.) thick operating on the plane of the upper surface of the lid. The shutter shall be so shaped and mounted that it rotates on the axis of the horizontal center of the lid between two stops so placed that when in one extreme position the openings *A*, *B*, and *C* of the lid are completely closed and when in the other extreme position these orifices are completely opened.

(*4*) ***Flame exposure device.***—The flame exposure device shall have a tip with an opening 0.027 in. (0.069 cm.) to 0.031 in. (0.079 cm.) in diameter. The flame exposure device shall be equipped with an operating mechanism which, when the shutter is in the " open " position, depresses the tip so that the center of the orifice is between the planes of the under and upper surfaces of the lid proper at a point on a radius passing through the center of the larger opening *A* and approximately 0.1 in. (0.254 cm.) from the outer edge of the opening.

NOTE.—A pilot flame for automatic relighting of the exposure flame should be provided.

A bead 0.156 in. (0.397 cm.) in diameter, of some suitable material, may be mounted on the lid so that the size of the test flame can be regulated by comparison.

The mechanism operating the shutter should be of the spring type and constructed so that when at rest the shutter shall exactly close the three openings. When operated to the other extreme the three openings in the lid shall be exactly open and the tip of the exposure tube shall be fully depressed.

(*c*) ***Stove.***—Heat shall be supplied to the cup by means of a properly designed stove which is equivalent to an air bath. This stove shall consist of (1) an air bath and (2) a top plate on which the flange of the cup rests.

(*1*) ***Air bath.***—The air bath shall have a cylindrical interior 1.625 in. (4.128 cm.) to 1.656 in. (4.206 cm.) deep and a diameter not less than 0.125 in.

(0.317 cm.) nor more than 0.156 in. (0.396 cm.) greater than the outside diameter of the cup. The air bath may be either a flame heated metal casting or an electric resistance element.

NOTE.—If the heating element is a flame-heated metal casting it shall be so designed and used that the temperature of bottom and walls is approximately the same. On this account it should be not less than 0.25 in. (0.635 cm.) thick. The casting shall be designed so that products of combustion of the flame cannot pass up and in contact with the cup.

If the air bath is of the electric resistance type it shall be constructed so that all parts of the interior surface are heated equally. This necessitates an even distribution of resistance wire over bottom and walls and a method of construction such that heat is given out from the whole core of the resistance element rather than directly from the wire.

(*2*) ***Top plate.***—The top plate shall be of metal. The total distance from the upper surface of the plate to the bottom of the air bath shall exceed the distance from the under surface of the flange to the bottom of the cup by not less than 0.063 in. (0.160 cm.) nor more than 0.125 in. (0.317 cm.).

The top plate shall be mounted with an air gap between it and the air bath. The top plate may be attached to the air bath by means of three screws and spacing bushings. The spacing bushings should be of proper thickness to define the air gap which shall be not less than 0.125 in. (0.317 cm.) nor more than 0.187 in. (0.475 cm.). The spacing bushings shall be not more than 0.375 in. (0.952 cm.) in diameter.

(*d*) ***Thermometers.***—Two standard thermometers shall be used with the A. S. T. M. Pensky-Martens tester. The low range, " A. S. T. M. P.M. and Tag " thermometer shall be used for tests when the indicated reading falls within the limits 20° to 200° F. The " A. S. T. M. P.M. high " thermometer shall be used for tests when the indicated reading falls within the limits 230° to 700° F. For the range 200° to 230° F. either thermometer may be employed, depending on the convenience of the operator. The thermometers shall comply with the requirements given in Tables I and II. The Low Range " A. S. T. M. P.M. and Tag " thermometer specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −7° to +110° C. or +20° to +230° F., respectively. The high range " A. S. T. M. P.M. high " thermometer specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being 90° to 370° C. or 200° to 700° F., respectively.

Thermometers shall be mounted so that the bottom of the bulb is 1.75 in. (4.445 cm.) below the level of the rim of the cup (which corresponds to the level of the lower surface of the portion of the lid inside the rim).

TABLE I.—SPECIFICATIONS FOR LOW RANGE "A. S. T. M. P.M. AND TAG" THERMOMETER [53]

TYPE: Etched stem, glass.
LIQUID: Mercury.
RANGE AND SUBDIVISION: −7° to +110° C. in 0.5° C. or +20° to +230° F. in 1° F.
TOTAL LENGTH: 273 to 277 mm. (10.75 to 10.92 in.).

[53] The low range "A. S. T. M. P.M. and Tag" thermometer is the same instrument as that specified for use with the Tag closed tester, see the Standard Method of Test for Flash Point by Means of Tag Closed Tester (A. S. T. M. Designation: D 56) of the American Society for Testing Materials, see 1936 Book of A. S. T. M. Standards, Part II.

STEM: Plain front, enamel back, suitable thermometer tubing. Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).

BULB: Corning normal or equally suitable thermometric glass.
Length, 9 to 13 mm. (0.35 to 0.51 in.).
Diameter, not greater than stem.

DISTANCE TO −7° C. OR +20° F. LINE FROM BOTTOM OF BULB: 75 to 90 mm. (2.93 to 3.54 in.).

DISTANCE TO 110° C. OR 230° F. LINE FROM TOP OF THERMOMETER: 25 to 40 mm. (0.98 to 1.57 in.).

EXPANSION CHAMBER: To permit heating the thermometer at least 50° C. (90° F.) above highest temperature on scale.

FILLING ABOVE MERCURY: Nitrogen gas.

TOP FINISH: Glass ring.

GRADUATION: All lines, figures, and letters clear cut and distinct. The whole degree Centigrade lines or the first and each succeeding 5° F. line to be longer than the remaining lines. Graduations to be numbered at each multiple of 5° C. or 10° F.

IMMERSION: 57 mm. or 2¼ in. The words "57-mm. immersion" on Centigrade or "2¼-in. immersion" on Fahrenheit thermometers and a line around the stem 57.0 mm. or 2.25 in. above the bottom of the bulb shall be etched on the thermometer.

SPECIAL MARKING: "A. S. T. M. P.M. and Tag.," a serial number and the manufacturer's name or trade mark, shall be etched on the stem.

SCALE ERROR: The error at any point of the scale when the thermometer is standardized as provided below shall not exceed 0.5° C. or 1° F., respectively.

STANDARDIZATION: The thermometer shall be standardized at the ice point and at intervals of approximately 30° C. or 50° F. for 57-mm. or 2¼-in. immersion and for the following temperatures of the emergent mercury column:

Thermometer Reading		Average Temperature of Emergent Mercury Column	
20° C.	70° F.	20° C.	70° F.
40° C.	100° F.	31° C.	86° F.
70° C.	150° F.	40° C.	104° F.
100° C.	212° F.	48° C.	118° F.

CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. P.M. and Tag., −7° to +110° C." or "A. S. T. M. P.M. and Tag., +20° to +230° F." according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

TABLE II.—SPECIFICATIONS FOR HIGH RANGE "A. S. T. M. P.M. HIGH" THERMOMETER

TYPE: Etched stem, glass.

LIQUID: Mercury.

RANGE AND SUBDIVISION: 90° to 370° C. in 2° C. or 200° to 700° F. in 5° F.

TOTAL LENGTH: 273 to 277 mm. (10.75 to 10.92 in.).

STEM: Plain front, enamel back, suitable thermometer tubing. Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).

BULB: Corning normal or equally suitable thermometric glass.
Length, not over 10 mm. (0.39 in.).
Diameter, not greater than stem.

DISTANCE TO 93° C. OR 200° F. LINE FROM BOTTOM OF BULB: 75 to 90 mm. (2.93 to 3.54 in.).

DISTANCE TO 371° C. OR 700° F. LINE FROM TOP OF THERMOMETER: 25 to 40 mm. (0.98 to 1.57 in.).

FILLING ABOVE MERCURY: Nitrogen gas.

TOP FINISH: Glass ring.

GRADUATION: All lines, figures, and letters clear cut and distinct. The first and each succeeding 10° C. or 25° F. line to be longer than the remaining lines. Graduations to be numbered at multiples of 20° C. or 50° F.

IMMERSION: 57 mm. or 2¼ in. The words "57-mm. immersion" on Centigrade thermometers or "2¼-in. immersion" on Fahrenheit thermometers and a line around the stem 57.0 mm. or 2.25 in. above the bottom of the bulb shall be etched on the thermometer.

SPECIAL MARKING: "A. S. T. M. P.M. High," a serial number and the manufacturer's name or trade mark shall be etched on the stem.

SCALE ERROR: The error at any point of the scale when the thermometer is standardized as described below shall not exceed 1° C. or 2½° F.

STANDARDIZATION: The thermometer shall be standardized at intervals of approximately 50° C. or 100° F. for 57-mm. or 2¼-in. immersion and for the following temperatures of the emergent mercury column:

Thermometer Reading		Average Temperature of Emergent Mercury Column	
100° C.	200° F.	61° C.	140° F.
150° C.	300° F.	65° C.	149° F.
200° C.	400° F.	71° C.	160° F.
250° C.	500° F.	78° C.	175° F.
300° C.	600° F.	87° C.	195° F.
350° C.	700° F.	99° C.	220° F.

TEST FOR PERMANENCY OF RANGE: After being subjected to a temperature between 360° and 370° C. or 680° and 700° F. for 24 hours, the accuracy shall be within the limit specified. The test shall be made under the immersion conditions specified for this thermometer.

CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. P.M. High, 90° to 370° C." or "A. S. T. M. P.M. High, 200° to 700° F." according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

Procedure.—(*a*) All parts of the cup and its accessories shall be thoroughly clean and dry before the test is started. Particular care shall be taken to avoid the presence of any gasoline or naphtha used to clean the apparatus after a previous test.

(*b*) The cup shall be filled with the oil to be tested up to the level indicated by the filling mark.

(*c*) The lid shall be placed on the cup and the latter set in the stove. Care shall be taken to have the locating devices properly engaged. The thermometer shall be inserted. If it is known that the oil will flash above 220° F. the "A. S. T. M. P.M. High" thermometer may be selected; otherwise, it is preferable to start with the "A. S. T. M. P.M. and Tag" thermometer and change in case a temperature of 220 to 230° F. is reached.

(*d*) The test flame shall be lighted and adjusted so that it is of the size of a bead $\frac{5}{32}$ in. (3.97 mm.) in diameter.

(*e*) Heat shall be supplied at such a rate that the temperature read on the

thermometer increases not less than 9 nor more than 11° F. per minute. The stirrer shall be turned at a rate of from 1 to 2 revolutions per second.

(*f*) Application of the test flame shall be made at each temperature reading which is a multiple of 2° F. up to 220° F. For the temperature range above 220° F., application shall be made at each temperature reading which is a multiple of 5° F. The first application of the test flame shall be made at a temperature at least 30° F. below the actual flash point. Application of the test flame shall be made by operating the device controlling the shutter and test flame burner so that the flame is lowered in one-half second, left in its lowered position for one second, and quickly raised to its high position. Stirring shall be discontinued during the application of the test flame.

Flash Point.—The flash point is taken as the temperature read on the thermometer at the time of the flame application that causes a distinct flash in the interior of the cup. The true flash must not be confused with the bluish halo that sometimes surrounds the test flame for the applications preceding the one that causes the actual flash.

Barometric Pressure.—The barometric pressure shall be observed and recorded. No corrections shall be made except in case of dispute when the flash point figure shall be corrected according to the following rule:

For each inch (25 mm.) below 29.92 in. (760 mm.) barometric reading add 1.6° F. to the flash point.

For each inch (25 mm.) above 29.92 in. (760 mm.) barometric reading subtract 1.6° F. from the flash point.

Determination of Flash Point of Cut-Back Asphalts and Other Viscous Materials and Suspensions of Solids.—The apparatus shall consist of the following:

(*a*) Pensky-Martens tester as described above except that the stirrer shall be mechanically operated to stir in a downward direction at a speed of 70 to 80 r.p.m.

(*b*) Low-range thermometer as specified in Table I.

Procedure.—The material to be tested and the tester shall be brought to a temperature 30° F. lower than the estimated flash point. The air space between the cup and the interior of the air bath shall be completely filled with water at the temperature of the tester and material. The temperature shall be raised throughout the duration of the test at a rate of not less than 4 nor more than 6 F. per min. With the exception of this requirement for rate of heating and the rate of stirring of 70 to 80 r.p.m., specified in Section 6 (*a*), the procedure shall be the same as that prescribed in the Standard Method of Test for Flash Point by Means of the Tag Closed Tester (A. S. T. M. Designation: D 56) of the American Society for Testing Materials.[54]

Accuracy.—Duplicate tests should not differ by more than 5° F.

[54] 1936 Book of A. S. T. M. Standards, Part II.

STANDARD METHOD OF TEST FOR FLASH POINT BY MEANS OF THE TAG CLOSED TESTER [55]

A. S. T. M. Designation: D 56–36 [56]

Scope.—The Tag closed tester shall be used for determining the flash point of all mobile liquids flashing below 175° F., with the exception of products classed as fuel oil which are preferably tested with the Pensky-Martens Closed Tester as described in the Standard Method of Test for Flash Point by Means of the Pensky-Martens Closed Tester (A. S. T. M. Designation: D 93) of the American Society for Testing Materials.[57] Provision is made in later Sections of this method for determining the flash point of lacquer solvents or diluents of low flash points.

Tag Closed Tester, a diagram of which appears in Fig. 252, shall conform to the following dimensional requirements within the permissible variations shown:

Dimensions	Inches			Centimeters		
	Minimum	Normal	Maximum	Minimum	Normal	Maximum
Depth of water surface below top of cup	$1\frac{5}{64}$	$1\frac{3}{32}$	$1\frac{7}{64}$	2.74	2.78	2.82
Depth of oil surface below top of cup	$1\frac{9}{64}$	$1\frac{5}{32}$	$1\frac{11}{64}$	2.90	2.94	2.98
Depth of top of bulb of oil thermometer when in place below top of cup	$1\frac{9}{32}$	$1\frac{5}{16}$	$1\frac{11}{32}$	3.25	3.33	3.41
Inside diameter of oil cup at top	$2\frac{12}{100}$	$2\frac{1}{8}$	$2\frac{13}{100}$	5.39	5.40	5.41
Diameter of bead on top of cover	$\frac{9}{64}$	$\frac{5}{32}$	$\frac{11}{64}$	0.36	0.40	0.44
Weight of oil cup	—	—	—	—	67 to	69 g.

The plane of underside of cover shall be between the top and bottom of the burner tip when the tip is fully depressed.

Thermometer.—Two thermometers are required, one for measuring the temperature of the sample under test, the other for measuring the temperature of the bath. Each of these thermometers shall conform to the following requirements. These specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −7° to +110° C. or +20° to +230° F., respectively:

Type: Etched stem, glass.
Liquid: Mercury.
Range and Subdivision: −7° to +110° C. in 0.5° C. or +20° to +230° F. in 1° F.
Total Length: 273 to 277 mm. (10.75 to 10.92 in.).

[55] Under the standardization procedure of the Society, this method is under the joint jurisdiction of A. S. T. M. Committee D-1 on Paint, Varnish, Lacquer, and Related Products, and Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[56] This method is issued under the fixed designation D 56; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1918; Adopted in Amended Form, 1919; Revised, 1921, 1936.

[57] 1936 Book of A. S. T. M. Standards, Part II, p. 897.

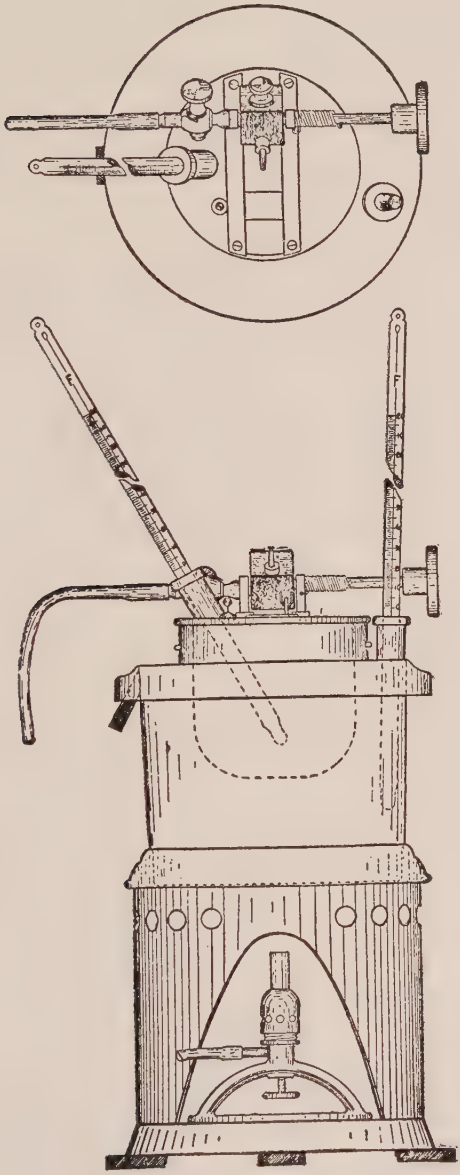


Fig. 252.—A. S. T. M. Tag Closed Tester. (Arranged for Use of Gas.)

Stem: Plain front, enamel back, suitable thermometer tubing. Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).

Bulb: Corning normal or equally suitable thermometric glass.
Length, 9 to 13 mm. (0.35 to 0.51 in.).
Diameter, not greater than stem.

Distance to −7° C. or +20° F. Line from Bottom of Bulb: 75 to 90 mm. (2.93 to 3.54 in.).

Distance to 110° C. or 230° F. Line from Top of Thermometer: 25 to 40 mm. (0.98 to 1.57 in.).

Expansion Chamber: To permit heating the thermometer at least 50° C. (90° F.) above highest temperature on scale.

Filling above Mercury: Nitrogen gas.

Top Finish: Glass ring.

Graduation: All lines, figures, and letters clear cut and distinct. The whole degree Centigrade lines or the first and each succeeding 5° F. line to be longer than the remaining lines. Graduations to be numbered at each multiple of 5° C. or 10° F.

Immersion: 57 mm. or 2¼ in. The words "57-mm. immersion" on Centigrade or "2¼-in. immersion" on Fahrenheit thermometers and a line around the stem 57.0 mm. or 2.25 in. above the bottom of the bulb shall be etched on the thermometer.

Special Marking:[58] "A. S. T. M. P.M. and Tag.," a serial number and the manufacturer's name or trade mark shall be etched on the stem.

Scale Error: The error at any point of the scale when the thermometer is standardized as provided below shall not exceed 0.5° C. or 1° F., respectively.

Standardization: The thermometer shall be standardized at the ice point and at intervals of approximately 30° C. or 50° F. for 57-mm. or 2¼-in. immersion and for the following temperatures of the emergent mercury column:

Thermometer Reading		Average Temperature of Emergent Mercury Column	
20° C.	70° F.	20° C.	70° F.
40° C.	100° F.	31° C.	86° F.
70° C.	150° F.	40° C.	104° F.
100° C.	212° F.	48° C.	118° F.

Case: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. P.M. and Tag., −7° to +110° C." or "A. S. T. M. P.M. and Tag., +20° to +230° F." according to the type of thermometer.

Note.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

Procedure.—(*a*) The test shall be performed in a room or compartment darkened sufficiently to permit ready detection of the flash.

(*b*) Care shall be taken to have the tester level and steady. It shall be surrounded on three sides by an enclosure for protection from drafts. (A shield 18 in. square and 24 in. in height, open in front, is suggested. Tests made in a laboratory hood or near ventilators are not to be relied upon.)

(*c*) Gas may be used for the test flame and for heating the water bath. If gas is not available for the test flame, a wick of cotton cord may be inserted

[58] This thermometer is identical with the low range instrument specified for use with the A. S. T. M. Pensky-Martens Closed Tester and described in the Standard Method of Test for Flash Point by Means of the Pensky-Martens Closed Tester (A. S. T. M. Designation: D 93) of the American Society for Testing Materials, see 1936 Book of A. S. T. M. Standards, Part II, p. 897.

in the burner tip, a small quantity of cotton waste placed in the oil chamber to which the burner tip is attached and the chamber filled with signal, sperm, or lard oil. An alcohol lamp may be used for heating the water bath as a substitute for gas.

The water bath thermometer shall be placed in the collar provided for it and the bath filled with water until it overflows. The temperature of the water in the bath shall be such that when testing is started it will be at least 20° F. (11° C.) below the probable flash point of the oil to be tested.

The oil cup shall be placed in its proper position in the water bath and 50 ml. of the oil to be tested shall be measured into it, using an accurate graduate or other measuring device for the purpose. The temperature of the oil shall be at least 20° F. (11° C.) below its probable flash point when the test is started. Air bubbles on the surface of the oil shall be destroyed, and the cover with the flash point thermometer in place shall then be properly attached to the bath collar. The test flame shall be lighted, the flame being adjusted to the size of the small white bead on the cover.

The gas burner or alcohol lamp shall be centrally placed in the base of the tester and lighted. The flame shall be so adjusted that the temperature of the oil in the cup rises at the rate of 1.8° F. (1° C.) per min. as closely as possible, but in any case not faster than 2° F. (1.1° C.) nor slower than 1.6° F. (0.9° C.) per min.

(*a*) The barometric pressure shall be recorded. If a barometer is not available, the figure may be obtained from the nearest Weather Bureau Station and an appropriate correction made for difference in altitude between such station and the laboratory.

(*b*) The initial temperature of the oil shall be recorded.

(*c*) When the temperature of the oil is 9° F. (5° C.) below its probable flash point, the knob on the cover shall be turned in such a manner as to introduce the test flame into the vapor space of the cup, and *immediately* turned back again. The time consumed in turning the knob down and back shall be about one full second, or the time required to pronounce distinctly the words " thousand and one."

(*d*) The time at which the first introduction of the test flame is made and the temperature of the oil shall be recorded.

(*e*) The application of the test flame shall be repeated after each 1° F. (0.5° C.) rise in temperature of the oil until a distinct flash in the interior of the cup is observed. The true flash must not be confused with the bluish halo which sometimes surrounds the test flame during applications immediately preceding the actual flash.

(*f*) The time and the temperature of the oil when the flash point is reached shall be recorded.

Repeat Tests.—(*a*) If the rise in temperature of the oil from the time of making the first introduction of the test flame to the time at which the flash point is observed was more rapid than 2° F. (1.1° C.), or slower than 1.6° F. (0.9° C.) per min., the test shall be repeated, adjusting the gas burner or alcohol lamp to the proper rate of heating.

(*b*) It is not necessary to turn off the test flame with the small regulating valve on the cover; it may be left adjusted to the proper size of flame.

(*c*) After completing the preliminary test to determine the approximate

flash point, the burner or lamp shall be removed, the oil cover lifted and the thermometer bulb carefully wiped off. The oil cup shall be removed, emptied, and carefully wiped until dry.

(*d*) The temperature of the bath shall be lowered by the addition of cold water until it is 15° F. (8° C.) below the flash point of the oil as shown by the preliminary test.

(*e*) The oil cup shall be replaced and a fresh 50-ml. sample measured into it. The test procedure, as described above, shall then be repeated, introducing the test flame for the first time, however, when the oil temperature is 10° F. (5.5° C.) below the flash point obtained in the preliminary test.

(*f*) Oil which has once been subjected to the flash test shall be discarded.

(*g*) If test is to be repeated, a fresh sample shall be used.

Average Value of Flash Point.—If two or more determinations agree within 1° F. (0.5° C.), the average of these results, corrected for barometric pressure, shall be considered the flash point. If two determinations do not check within 1° F. (0.5° C.), a third determination shall be made and, if the maximum variation of the three tests is not greater than 2° F. (1° C.), their average, after correcting for barometric pressure, shall be considered the flash point.

Correction for Barometric Pressure.—Correction for barometric pressure shall be made only in cases of dispute or when the barometer reading varies more than ½ in. (13 mm.) from the standard pressure of 29.92 in. (760 mm.). When the barometer reading is below this standard pressure, add to the thermometer reading 1.6° F. (0.9° C.) for each 1 in. (25 mm.) of barometer difference to obtain the true flash point. When the barometer reading is above the standard pressure, deduct 1.6° F. (0.9° C.) for each 1 in. (25 mm.) of barometer difference to obtain the true flash point.

Determination of Flash Point of Lacquer Solvents or Diluents of Low Flash Point

Apparatus.—The apparatus shall consist of the following:

(*a*) ***Flash Point Tester.***—As described under "Tag Closed Tester."

(*b*) ***Thermometer.***—For determining flash points below 40° F. (4.4° C.), suitable thermometers of low range shall be used. These thermometers shall conform to the requirements as given above except that the ranges shall be 0° F. to 120° F. or −20° C. to +50° C. These thermometers may not be used in the testing of materials flashing above 70° F. (21.1° C.).

Procedure.—The procedure to be followed shall be the same as that described previously, except that in determining flash points below 40° F. (4.4° C.) the bath shall be filled with brine or other low-freezing liquid instead of water.

Viscosity is determined with the Saybolt Furol viscosimeter, p. 1719.

Sulfur [59] (A. S. T. M. Method D 129–34)

This method shall be used for the determination of sulfur in petroleum oils which cannot be burned completely in a wick lamp.

Apparatus.—The oxygen bomb shall have a capacity of not less than 300 ml. and shall be of a design or construction such that no leaks shall occur at any

[59] Tech. Paper 323B. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

pressure or temperature generated during the test, and such that when the bomb is open the liquid contents can be easily and completely drained. The inner surfaces shall be of materials that are chemically and physically resistant to the process or products of combustion. The gaskets, insulating materials, etc., shall be, as far as possible, physically and chemically resistant and in no event shall they undergo any reaction which would increase or decrease the sulfur content of the bomb liquors.

The oil cup shall be of platinum, glazed silica, or other suitable material, with a capacity of not less than 2.5 ml. nor more than 5 ml.

If a platinum oil cup is used, the fuse wire shall be of platinum; if a glazed silica oil cup is used, the fuse wire may be of either platinum or iron. No. 35 (B. and S. gage) is a convenient size.

(*a*) The distilled water and all reagents should be sulfur free, but when it is necessary to employ reagents not sulfur free, blanks shall be run and the figures thus obtained used to correct the results of actual determinations.

(*b*) The barium chloride solution shall contain 100 grams of $BaCl_2 \cdot 2H_2O$ per liter.

Procedure.—(*a*) Twenty ml. of distilled water shall be placed in the bottom of the bomb. From 0.6 to 0.8 gram of the oil to be tested shall be placed in the weighed oil cup and the weight of this charge shall be determined to an accuracy of at least ± 0.002 gram. The cup shall be placed in the proper position in the bomb, the ignition mechanism arranged and the bomb closed. Oxygen shall be admitted slowly until a pressure is reached as indicated by the following table:

Capacity of Bomb, ml.	Minimum Gage Pressure, Atmospheres
300 to 350	40
350 to 400	35
400 to 450	30
450 to 500	27.5
Above 500	25

The leads from the firing circuit shall be attached, the bomb placed in a bucket of cold water, and ignited. The bomb shall be allowed to stand in the water for 10 minutes and shall then be removed. The valve of the bomb shall be opened, allowing the gas to escape at an approximately even rate so that the pressure is reduced to atmospheric in not less than 1 minute. The bomb shall be opened, and all parts of its interior, including the oil cup, rinsed with a fine jet of distilled water. All washings, which should not amount to more than 350 ml., shall be collected in a beaker. Particular care should be taken not to lose, by splashing or otherwise, any of the liquid contents of the bomb. The washings shall be filtered through a washed " qualitative " filter paper. The filter shall be washed thoroughly. Two ml. of concentrated HCl and 10 ml. of saturated bromine water shall be added to the filtrate. The solution shall be evaporated to about 75 ml. on a steam bath or hot plate. Ten ml. of hot barium chloride solution shall be added in a fine stream or dropwise to the hot solution, stirring during the addition and for 2 minutes afterwards. The solution shall be allowed to stand over night, or shall be kept hot for 1 hour on the steam bath or hot plate, allowing the precipitate to settle for another hour while cooling. The supernatant liquid shall be filtered through an " ashless

quantitative" filter paper and the precipitate washed with water, first by decantation, then on the filter, till free from chloride. The paper and precipitate shall be transferred to a suitable weighed crucible, dried at low heat till moisture is evaporated, the paper charred (without flaming), and finally ignited at a good red heat till the precipitate is just burned white. A satisfactory means of accomplishing these operations is to place the crucible containing the wet filter paper in a cold electric muffle furnace and to turn on the current. Drying, charring, and ignition will usually occur at the desired rate.

(*b*) After ignition is complete, the crucible shall be allowed to cool to room temperature and weighed. The use of a desiccator is not recommended.

(*c*) From the increase in weight of the crucible the percentage of sulfur shall be calculated from the formula:

$$\text{Percentage of sulfur} = \frac{\text{grams of } BaSO_4 \times 13.734}{\text{grams of oil used}}.$$

Accuracy.—The percentages of sulfur obtained by the same operator with the same apparatus should not differ by more than 0.02+0.04 A; while the percentages obtained by different operators should not differ by more than 0.02+0.08 A (A represents the average of percentages obtained).

The Jackson Turbidimeter can be used for rapid work.

Water and *Sediment* are determined as follows:

Water (A. S. T. M. Method D95–30) [60]

This method of test determines the water in a sample of bituminous material by distilling the sample with a volatile solvent. This method is suitable for a variety of materials but is especially applicable to petroleum, fuel oil, road oil, coal tar, water-gas tar, coke-oven tar, and other petroleum products or bituminous materials.

Apparatus.—The apparatus shall consist of a metal still or glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the still or flask. The trap serves to collect and measure the condensed water and to return the solvent to the still.

The type of distilling apparatus used is not an essential feature of this method, but glass has been generally used for petroleum products and the metal still for road materials and tars.

3. (*a*) The metal still (Fig. 253, *a*) shall be a vertical cylindrical vessel, preferably of copper, having a faced flange at the top to which the head is tightly attached by means of a clamp. The head shall be of metal, preferably of brass or copper, and be provided with a tubulation 1 inch in inside diameter.

(*b*) The glass flask (Fig. 253, *b*) shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

The burner used with the metal still shall be a ring gas burner 4 inches (100 mm.) in inside diameter. With the glass flask an ordinary gas burner or electric heater may be used as the source of heat.

The condenser shall be of the water-cooled, reflux, glass tube type, having a condenser jacket not less than 400 mm. (15¾ inches) in length with an

[60] Tech. Paper 323B. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

inner tube 12 to 16 mm. (½ to ⅝ inch) in diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30° from the vertical axis of the condenser.

The trap shall be made of well-annealed glass constructed in accordance with Fig. 253, *c*, and shall be graduated as shown from 0 to 10 ml. in 0.1 ml. divisions. The error of any indicated capacity shall not be greater than 0.05 ml.

The outside diameters should preferably be 2.5 to 3.5 mm. ($\frac{3}{32}$ to ⅛ inch) greater than the inside diameters specified.

(*a*) The solvent used when testing petroleum products or bituminous materials derived from petroleum shall be gasoline free from water and shall

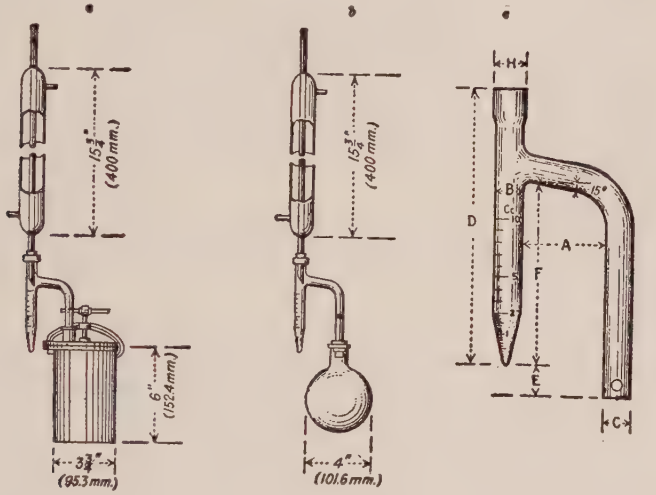

15¾" (400 mm.)
6" (152.4 mm.)
3¾" (95.3 mm.)
15¾" (400 mm.)
4" (101.6 mm.)
H
B
D
A
F
E
C
A— 45 to 55 mm. = 1¾" to 2⅛"
B—(Inside Diameter) 14 " 16 mm. = 9/16" " 5/8"
C—(Inside Diameter) 12 " 16 mm. = ½" " 5/8"
D— 150 " 170 mm. = 6" " 6¾"
E— 25 " 38 mm. = 1" " 1½"
F— 100 " 108 mm. = 4" " 4¼"
H— 18 " 19 mm. = 11/16" " ¾"

FIG. 253.—Apparatus for Determination of Water.

conform to the following distillation requirements, determined in accordance with the " Tentative method of test for distillation of gasoline, naphtha, kerosene, and similar petroleum products"; A. S. T. M.–D 86. Five percent shall distil at a temperature not below 194° F. (90° C.) nor above 212° F. (100° C.); 90% shall distil below 410° F. (210° C.).

(*b*) The solvent used when testing bituminous materials derived from coal tar, water-gas tar, etc., shall be a coal-tar naphtha or a light oil and shall conform to the following distillation requirements, determined in accordance with the " Tentative method of test for distillation of gasoline, naphtha, kerosene, and similar petroleum products"; A. S. T. M.–D 86, 98% shall distil between 248° F. (120° C.) and 482° F. (250° C.).

Sample.—The sample shall be thoroughly representative of the material to be tested and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement shall not be permitted.

NOTE.—The difficulties in obtaining proper representative samples for this determination are unusually great, so that the importance of sampling can not be too strongly emphasized.

Procedure.—When the sample to be tested contains less than 10% of water, exactly 100 ml. of the material to be tested shall be placed into the still or flask and thoroughly mixed with an equal volume of solvent by swirling, proper care being taken to avoid any loss of material. If the material is measured by volume, an accurate 100-ml. graduated cylinder shall be used and the contents transferred to the still by rinsing with one 50-ml. portion of solvent followed by two successive 25-ml. portions of solvent, the cylinder being allowed to drain each time. When the sample to be tested contains more than 10% of water, the volume of material used shall be decreased to that which will yield somewhat less than 10 ml. of water.

NOTE.—In special cases where the water content exceeds 10% and it is not desirable to reduce the size of the sample to that which will yield somewhat less than 10 ml. of water, a distilling tube receiver graduated from 0 to 25 ml. may be used. This tube shall be graduated from 0 to 2 ml. in 0.1 ml. from 2 to 5 ml. in 0.2 ml., and from 5 to 25 ml. in 0.5 ml.

The connections between the still or flask, trap, and condenser shall be made by means of tight-fitting corks as shown in Fig. 253 (*a* and *b*). The end of the condenser inserted in the trap shall be adjusted to that position which will allow the end to be submerged to a depth of not more than 1 mm. below the surface of the liquid in the trap after distillation conditions have been established. When the metal still is used, a heavy paper gasket moistened with the solvent shall be inserted between the lid and flange before attaching the clamp. A loose cotton plug shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

Heat shall then be applied and so regulated that the condensed distillate falls from the end of the condenser at the rate of from 2 to 5 drops per second. The ring burner used with the metal still should be placed about 3 inches above the bottom of the still at the beginning of the distillation and gradually lowered as the distillation proceeds.

The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. This operation usually requires less than an hour. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of distillation for a few minutes.

The volume of condensed water measured in the trap at room temperature multiplied by 100 and divided by the volume of the sample used shall be the percentage of water and shall be reported as "—per cent water by volume, *A. S. T. M. method.*"

Accuracy.—The accuracy to be expected with this method is that duplicate determinations of water should not differ from each other by more than one division on the trap.

Sediment

Apparatus.—Alundum (porous grade) thimbles,[61] 1 inch in diameter by 2¾ inches high, weighing not less than 15 nor more than 17 grams.

Extraction apparatus (see Fig. 254) of such construction that the thimble is completely surrounded by the vapor of the boiling solvent. *Siphon extractors must not be used.*

Procedure.—Place approximately 10 grams of the sample in the previously extracted and dried, accurately weighed thimble and weigh to ±0.01 gram, place in the extraction apparatus, and extract with 90% benzol until the solvent dropping from the thimble is colorless. Dry the thimble for 1 hour at 105° C., and weigh to ±0.0001 gram. Repeat the extraction until the weight of the dried thimble and sediment is constant.

NOTE—The rate of extraction shall be such that the mixture of oil and benzol in the thimble does not rise to within ¼ inch of the top.

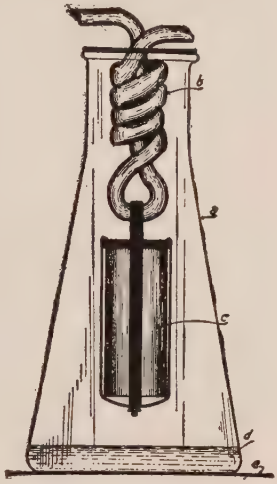


FIG. 254.—Extraction Apparatus for Determination of Sediment: *a*, Extraction flask; *b*, condenser; *c*, extraction thimble; *d*, solvent; *e*, top of hot plate.

Water and Sediment by Centrifuge (A. S. T. M. Method D 96–35) [62]

This method may be used for crude mineral oils and fuel oils. A centrifuge method for "Water and Sediment" is not entirely satisfactory because the amount of water obtained is nearly always lower than the actual water content. Nevertheless, on account of the wide use of the centrifuge for this purpose, it is desirable that the method of making the determination be standardized as far as possible. It must be clearly understood that the reading of the centrifuge tube includes both the sediment and the precipitated water. Accurate determination of water content, if desired, should be made in accordance with the Standard Method of Test for Water in petroleum products and other Bituminous Materials (A. S. T. M. D 95).

The sample shall be thoroughly representative of the material in question and the portion used for the test shall be thoroughly representative of the sample itself. Deviation from this rule shall not be permitted. The difficulties in obtaining representative samples for this determination are unusually great; hence the importance of sampling can not be too strongly emphasized.

Apparatus.—The centrifuge shall be capable of whirling at the required speed at least two 100-ml. centrifuge tubes filled with water. It shall be of sound design and rugged construction so that it may be operated without danger. The tube carriers shall be so designed that the glass centrifuge tubes may be cushioned with water, rubber, or other suitable material. The tube holders

[61] Alundum thimbles listed by the Norton Co., Worcester, Mass., as 5163 RA 98, have proved satisfactory.

[62] Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

shall be surrounded during the operation by a suitable metal shield or case, strong enough to eliminate danger if any breakage occurs.

The preferred form of centrifuge shall have a diameter of swing (tip to tip of whirling tubes) of 15 to 17 inches and a speed of at least 1500 r.p.m. or the equivalent. If the available centrifuge has a diameter of swing varying from these limits, it shall be run at the proper speed to give the same centrifugal force at the tips of the tubes as that obtained with the preferred form of centrifuge. The proper speed shall be calculated from the following formula in which d represents diameter of swing (tip to tip of whirling tubes) of the centrifuge used:

$$\text{r.p.m.} = 1500 \sqrt{\frac{16}{d}}.$$

The centrifuge tubes, A. S. T. M. types shown in Fig. 255, shall be made of suitable glass and thoroughly annealed. The total capacity shall be about 125 ml. and the mouth shall be suitably constricted for closing with a cork. The graduations shall be clear and distinct, reading upward from the bottom of the tube. Air-free distilled water at 20° C. (68° F.) shall be used for the calibration of tubes. The length and outside diameter are optional provided they do not conflict with the other requirements. The value of the divisions for each range with limits of error are given in the following tabulations for the A. S. T. M. Pear-Shaped Tube and A. S. T. M. Cone-Shaped Tube:

A. S. T. M. Pear-Shaped Tube

Range	Scale Division	Limit of Error	Numbered
0 to 3 ml.	0.1 ml.	0.05 ml.	1, 2, 3 ml.
3 to 5 "	0.5 "	0.2 "	4, 5 "
5 to 10 "	1.0 "	0.5 "	6, 8, 10 "
10 to 25 "	5.0 "	1.0 "	15, 20, 25 "
25 to 50 "	25.0 "	1.0 "	50 "
50 to 100 "	50.0 "	1.0 "	100 "

A. S. T. M. Cone-Shaped Tube

Range	Scale Division	Limit of Error	Numbered
0 to 0.1 ml.	0.05 ml.	0.02 ml.	—
0.1 to 0.3 "	0.05 "	0.03 "	—
0.3 to 0.5 "	0.05 "	0.05 "	½ ml.
0.5 to 1.0 "	0.1 "	0.05 "	1 "
1 to 3 "	0.1 "	0.1 "	2, 3 "
3 to 5 "	0.5 "	0.2 "	4, 5 "
5 to 10 "	1.0 "	0.5 "	6, 8, 10 "
10 to 25 "	5.0 "	1.0 "	15, 20, 25 "
25 to 100 "	25.0 "	1.0 "	50, 75, 100 "

The water or oil bath shall be of sufficient depth for immersing the centrifuge tubes in a vertical position to the 100-ml. mark. Means shall be provided for heating this bath to 120° F. (49° C.).

Procedure.—(*a*) Exactly 50 ml. of 90% benzol shall be measured into each of two centrifuge tubes and exactly 50 ml. of the oil to be tested shall then be added to each. The centrifuge tubes shall be tightly stoppered and shall be shaken vigorously until the contents are thoroughly mixed. The temperature of the bath shall be maintained at 120° F., and the centrifuge tubes shall be immersed therein to the 100-ml. mark for 10 minutes.

(*b*) The two centrifuge tubes shall then be placed in the centrifuge on opposite sides and shall be whirled at a rate of 1400 to 1500 r.p.m., or the equivalent, for 10 minutes. The combined volume of water and sediment at the bottom of each tube shall be read and recorded, estimating to 0.1 ml. if necessary. The centrifuge tubes shall then be replaced in the centrifuge, again whirled for 10 minutes, and removed for reading the volume of water and sediment as before.

This operation shall be repeated until the combined volume of water and sediment in each tube remains constant for three consecutive readings. In general, not more than four whirlings will be required.

The combined total volume of water and sediment shall be read on each tube, estimating to 0.1 ml. if necessary. The sum of the two readings shall be recorded as percentage of water and sediment, centrifuge method.

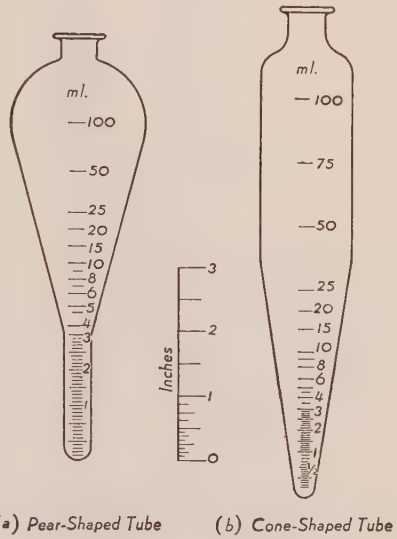


FIG. 255.—Centrifuge Tubes (A. S. T. M.).

Accuracy.—With care and proper attention to details, duplicate determinations of water and sediment by this method should not differ by more than 0.2 ml., provided the centrifuge tubes are accurate and readable to this degree.

Water by Centrifuge

Apparatus.—The apparatus shall be the same as in the preceding method.

Procedure.—Exactly 40 ml. of 90% benzol shall be measured into each of two centrifuge tubes and exactly 20 ml. of the oil to be tested shall then be added to each. The centrifuge tubes shall be tightly stoppered and shall be shaken vigorously until the contents are thoroughly mixed.

The two centrifuge tubes shall then be placed in the centrifuge on opposite sides and shall be whirled at a rate of 1400 to 1500 r.p.m., or the equivalent, for 10 minutes. The volume of water at the bottom of each tube shall be read and recorded, estimating to 0.1 ml. if necessary. The centrifuge tubes shall then be replaced in the centrifuge, again whirled for 10 minutes as before, and removed for reading the volume of water as before. This operation shall

be repeated until the volume of water in each tube remains constant for three consecutive readings.

The volume of water shall be read on each tube, estimating to 0.1 ml. if necessary, and the average percentage of water in the sample calculated.

Calorific Power.[63]—The calorific power of uncracked fuel oil can be found by the formula, Cal. Power = 17660 + (69 × A.P.I. gravity, ° Baumé). Of a cracked fuel oil, Cal. Power = 17780 + (54 × A.P.I. gravity, ° Baumé).

ANIMAL AND VEGETABLE OILS

The tests most commonly employed for the identification of these oils are as follows: specific gravity, refractive index, Valenta test, elaidin test, Maumené test, iodine number, and saponification value.

In addition, certain special and commercial tests are applied, as Bechi test, Baudouin test, free acid, spontaneous combustion, and drying test.

Specific Gravity.—This is usually determined either by the Westphal balance (page 1704) or by the *picnometer*.

A two-necked flask of 50 ml. capacity, having a thermometer carefully ground into one neck, the second one being a narrow tube bearing the mark, is most suitable. This is filled with the oil to be examined, cooled to 15.5° C.,[64] the excess of oil removed and weighed. If the weighings be made to 0.5 milligram and a correction applied for the expansion of the glass by the difference in temperature = 15.5 − 4 = 11.5° = −0.025% of the value obtained, the determination is accurate to 0.00002.[65]

For the determination of the specific gravity of small quantities of oil, satisfactory results can be obtained by weighing 1 or 5 ml. of the oil carefully measured from an accurately calibrated pipette. Or a mixture of alcohol and water can be made until a drop of oil will stay in any position in it, and its specific gravity determined.

Refractive Index.—This is of the same value as the determination of specific gravity: it has, however, the advantage that it is more rapid and uses only one or two drops of the oil.

The apparatus preferably employed is the Abbé refractometer, Fig. 256, the prisms of which are kept at constant temperature, usually 25° C., by circulating water.

The illuminating mirror should light the cross hairs and the telescope should be sharply focused on them.

[63] Faragher, Morrell & Truax, Ind. Eng. Chem., **21**, 933 (1929).

[64] Allen (Organic Analysis, 33) states that a correction of 0.00064 can be made for each variation of 1° C.

[65] Wright, J. Soc. Chem. Ind., **11**, 300, 1892.

The double prism is opened by means of the screw heads, and after carefully cleansing the prisms with cotton and ether, a drop or two of the oil placed on the horizontal surface of the fixed prism. The prisms are then tightly closed. The telescope is brought into the position shown and the sector is firmly held and the alidade (the moving part) moved forward until the field of vision shows the boundary between light and shade just intersecting the cross hairs.

By means of the screw on the right of the instrument this boundary line should be made as sharp as possible. The index of refraction is read off directly from the sector, using a lens if necessary; the reading is accurate to .0002.

After using, the prisms are again carefully cleansed and a piece of filter paper placed between them to prevent them from being scratched. The instrument is in correct adjustment when water at 18° gives a mean reading of 1.333. The temperature correction for oils and fats is 0.0004 for every degree rise.

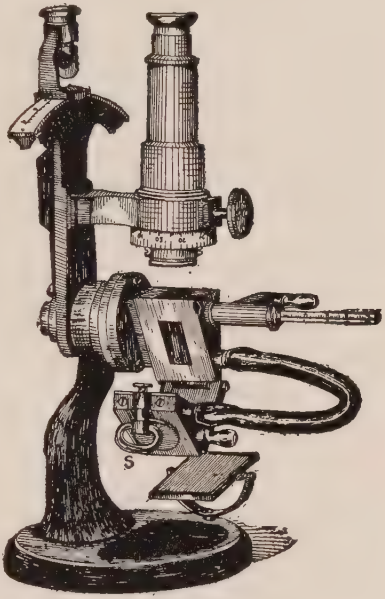


FIG. 256.—Refractometer.

Valenta Test.[66]—Although considered by some to be unreliable, yet as the indication given by this test may be of value, it is barely worth the trouble of execution. It depends upon the solubility of the oil in glacial acetic acid.

Enough oil is poured into a test-tube to fill it to the depth of about 1 in., the exact height being marked by the thumb; an equal quantity of glacial acetic acid is poured in, that is, until the acid reaches the point indicated by the thumb. A light thermometer is placed in the tube, and it is heated until the oil dissolves —shown by the liquid becoming homogeneous. The tube is now allowed to cool, and the point noted at which it begins to become thoroughly turbid.

Castor oil is soluble at ordinary temperatures, while rape-seed and other cruciferous oils are usually insoluble even at the boiling-point of the acid. The temperatures at which other oils become turbid are given on pages 1795 and 1796.

Elaidin Test.—Although this is not a quantitative test, yet its ease of application and the conclusions which may be drawn from it render it valuable. It depends upon the change of the liquid olein into its solid isomer elaidin, and is especially applicable to olive and lard oils.

Manipulation.—Five grams of the oil are weighed [67]—within 2 drops—into a cordial glass, 7 grams of nitric acid, specific gravity 1.34, are then weighed into it,[67] and two pieces of copper wire (0.6 to 1.0 gram) added. Place the glass in a pan of cold water at about 12° C., and stir with a short glass rod about 20 to 30

[66] Valenta, Dingler Polyt. J., **253**, 418; also J. Soc. Chem. Ind., **3**, 643, 1884.
[67] Not on the analytical balance.

turns, not only with a rotary movement, but also with an up-and-down motion, so as to mix the oil and the evolved gas thoroughly. When the wire has dissolved, add a second piece and stir as before. This second addition should furnish gas enough if the liquid has been kept cool and the stirring has been thorough.

At the end of the first hour, pure lard oil will usually show flakes of a wax-like appearance, and upon standing without disturbance and at the same temperature for another hour, the oil will have changed to a solid white cake hard enough to bear several ounces' weight, or admit of lifting the glass and contents by the glass rod.

Most of the fish and seed oils yield a pasty or buttery mass separating from a fluid portion, whereas olive, almond, peanut, lard, sperm and sometimes neat's-foot oil, yield a solid cake.

Instead of using nitric acid and copper, sulfuric acid of 46° Baumé, containing a little nitric acid and saturated at 0° C. with nitric oxide, may be employed.

A test should always be made at the same time with an oil of undoubted purity.

Notes.—If the oil be stirred too much or too frequently, or is too warm, it has no opportunity to form a hard cake.

Hübl states that all attempts to make the test a quantitative one have resulted in failure.

Mercury can be used instead of copper.

Cailletet's method,[68] in which a smaller quantity of oil is used, and sulfuric and nitric acids allowed to act upon it in a boiling water bath, cannot, in the experience of the writer, be depended upon to give reliable results.

Maumené Test.[69]—While this, like the preceding, is not a quantitative test, yet the indications afforded by it are of more value in many cases than those obtained by quantitative methods, as, for example, the saponification value. It depends upon the heat developed by the mixing of the oil with strong sulfuric acid. This takes place in a small beaker 7½ to 9 cm. deep and of 150 ml. capacity, packed in an agate-ware cup with dry felt or cotton waste packing.

Manipulation.—Fifty grams of the oil are weighed [70] into the beaker to within 2 drops, and its temperature noted by a thermometer. Ten ml. of sulfuric acid are now run gradually into the oil—allowing the graduate to drain five seconds—the mixture being stirred at the same time with the thermometer, and the stirring continued until no further increase in temperature is noted. The highest point at which the thermometer remains constant for any appreciable time is observed, and the difference between this and the initial temperature is the " rise of temperature." This varies with the strength of the acid employed, and to secure uniformity [71] the results should be expressed by dividing the rise of temperature with the oil by the rise of temperature with water, and multiplying by one hundred. This is called the " specific temperature reaction." The rise of temperature with water is determined in the same manner as with oil, using the same vessel.

[68] Milliau, J. Am. Chem. Soc., **15**, 156, 1893.

[69] SO_2Cl gives similar results.

[70] Not on the analytical balance.

[71] Tortelli, J. Soc. Chem. Ind., **23**, 668, 1904, is unable to secure uniformity in this way.

NOTES.—In performing this test it is important that the oil and acid be of the same temperature, attained by keeping them beside each other.

The strength of acid should be as far as possible the same; it should be determined not by specific gravity, but by titration, as 100% and 94.3% acid have the same specific gravity.

For concordant results the conditions should be the same, and the same apparatus should be used. In case the test is to be applied to a drying oil, it should be diluted one-half with a mineral oil, 25° paraffin, for example, thoroughly mixing them. The "rise of temperature" is then, the rise of temperature of mixture minus half the rise of temperature of 50 grams of mineral oil, multiplied by 2.

It is advisable to make a test at the same time with an oil of known purity. Results should agree within 2%. By the use of the Hübl formula, page 1769, substituting thermal values, results comparable with those obtained with the iodine value can be obtained.

Sherman, Danziger, and Kohnstamm [72] have studied this method with the idea of eliminating the errors. Rather than dilute the oil with a mineral oil they dilute the acid, using one of 89%. The results obtained are a little lower for vegetable oils and a little higher for animal oils than those usually found with the strong acid as employed by Thomson and Ballantyne. Mitchell [73] uses an inert diluent—carbon tetrachloride—in a vacuum-jacketed tube and one-fifth the quantities; all oils are diluted. He finds that the results obtained are in close agreement with the bromine thermal values; further, that the test may be of use in determining the degree of oxidation of fats and oils, the figures becoming greater with the age of the oil.

Data upon various oils will be found on pages 1795–1796.

References

Maumené, Compt.-Rend., **35**, 572, 1852.
Ellis, J. Soc. Chem. Ind., **5**, 361, 1886.
Thomson and Ballantyne, J. Soc. Chem. Ind., **10**, 234, 1891.
Richmond, Analyst, **20**, 58, 1895.
Munroe, Am. Pub. Health Ass'n, **10**, 236, 1884.

Iodine Number or Value.—This is the percentage of iodine absorbed by an oil; the method depends upon the fact that different oils absorb different amounts of the halogens; the process is mainly one of addition, although small quantities of substitution products are formed. For example, the unsaturated body olein, $(C_{17}H_{33}COO)_3C_3H_5$, when brought in contact with iodine takes up 6 atoms and forms the ***addition product,*** di-iodo stearin, $(C_{17}H_{33}I_2COO)_3C_3H_5$. Palmitin, $(C_{15}H_{31}COO)_3C_3H_5$, when similarly treated, forms no addition product, but a small quantity of the ***substitution product,*** iodo-palmitin, $(C_{15}H_{30}ICOO)_3H_5$, and the hydrogen displaced unites with the iodine to form hydriodic acid. The quantity of hydriodic acid thus formed is a measure of the amount of substitution.[74]

1. Hanus's Method.[75] *Manipulation.*—From 0.12 to 0.15 gram of a drying oil, 0.2 and 0.3 gram of a non-drying oil, or 0.6 to 0.7 gram of a solid fat, is accurately weighed into a ***dry*** 200-ml. bottle. This should be of colorless glass and be provided with a well-ground stopper. This is best effected by pouring out about 5 grams of the oil into a No. 1 beaker containing a short stirring rod, and setting it into a watch-glass upon the pan of the analytical balance. The whole system is weighed, the beaker removed, and several drops of oil transferred to the bottle by dropping down the rod, being careful that no oil touches the neck.

[72] J. Am. Chem. Soc., **24**, 266, 1902.
[73] Analyst, **26**, 169, 1901.
[74] McIlhiney, J. Am. Chem. Soc., **16**, 275, 1894.
[75] This is the official A. S. T. M. method.

Eight drops are approximately 0.2 gram. The beaker is replaced in the watch-glass and the system again weighed, the difference in weight being the amount of oil in the bottle.

The oil is dissolved in 10 ml. of chloroform, 30 ml. of the iodine solution (Reagents) added—best from a burette—and allowed to stand with occasional shaking for exactly thirty minutes; with oils of an iodine number of less than 100, ten minutes suffices; 10 ml. of potassium iodide solution are added; shake thoroughly, add 100 ml. water, washing down any iodine on the stopper. Titrate the excess of iodine with N/10 sodium thiosulfate, adding the latter gradually, with constant shaking, until the yellow color of the iodine has almost disappeared. Add a few drops of starch solution, shake thoroughly to dissolve out the iodine from the chloroform solution, and titrate to the disappearance of the blue color. The blue color returns after a few minutes but the end-point is that of its first disappearance.

At the same time at which the oil is prepared, two " blanks " should be prepared similarly in every way to the actual tests, except in the addition of the oil, and treated in every respect like them; the strength of the thiosulfate solution should also be determined the same day on which this test is carried out.

Standardization of the Thiosulfate Solution.—Ten ml. of potassium iodide and 100 ml. of water are poured into the Erlenmeyer flask; 20 ml. of the bichromate solution, equivalent to 0.2 gram of iodine, are now measured in with a pipette, and to this 5 ml. of concentrated hydrochloric acid added and the mixture shaken for three minutes. It is now titrated with the thiosulfate solution until the yellow color of the iodine has almost disappeared; starch paste is now added, and the titration continued until the deep-blue color of the solution changes to a sea-green—due to $CrCl_3$,—which is usually brought about by the addition of a single drop.

The reactions involved are:

$$K_2Cr_2O_7+14HCl=2CrCl_3+2KCl+7H_2O+3Cl_2;$$
$$3Cl_2+6KI=6KCl+3I_2;$$
$$6Na_2S_2O_3+3I_2=3Na_2S_4O_6+6NaI.$$

Notes.—Wijs [76] uses iodine chloride instead of bromide; it is more troublesome to prepare and gives results about 1.2 points higher.[77] Either of these methods has the advantage over Hübl's—first, that the solutions keep better, remaining practically unchanged for several months; secondly, that the action is about sixteen times as rapid, it being completed in fifteen minutes; thirdly, that the solutions are cheaper.

Acetic acid cannot be displaced by carbon tetrachloride as a solvent, as the last traces of iodine are difficult to remove from it. The acetic acid used should be at least 99.5% and show no reduction with potassium bichromate and sulfuric acid.

This method has been referred by Gill and Simms, J. Ind. Eng. Chem. ***13***, 547, so that a single drop of oil 0.03 gm. suffices for a test.

2. Hübl's Method. *Manipulation.*—The oil is weighed out as in 1, into 300-ml. bottles, except that about 25% more may be used.

The oil is now dissolved in 10 ml. of chloroform, 30 ml. of iodine and mercuric chloride solution added, the bottle placed in a dark closet, and allowed to stand, with occasional gentle shaking, for four hours. If the solution becomes

[76] Berichte, **31**, 752, 1898.
[77] Tolman and Munson, J. Am. Chem. Soc., **25**, 244, 1903.

nearly decolorized after two hours, an additional quantity should be added. One hundred ml. of distilled water and 20 ml. of potassium iodide are added to the contents, and the excess of iodine titrated with sodium thiosulfate. If at this point a red precipitate (HgI_2) is formed, more potassium iodide should be added. As the chloroform dissolves some of the iodine, the titration can proceed until the chloroform layer is nearly colorless, then the starch solution is added, and the operation continued to the disappearance of the blue color.

" Blanks " should be titrated as with the foregoing process, page 1768.

NOTES.—The method was proposed by Cailletet in 1857, made use of by Mills and Snodgrass [78] in 1883, using, however, bromine and carbon bisulfide, and described in almost its present form by Hübl.[79] The chief factors in its execution are (1) strength of the iodine solution; (2) the quantity used; and (3) the length of its time of action.

1. *The Strength of Iodine Solution.* According to Hübl's original memoir, the solutions can be kept indefinitely when mixed.

Fahrion [80] states that the solution deteriorated as much as from 17 to 23% in eight days. Ballantyne [81] confirms the deterioration, but finds it much less, 5 to 8% in thirty-eight days. This weakening of the solution is probably due to the hydriodic acid formed by the action of the iodine upon the alcohol.[82]

The mercuric chloride acts apparently as a carrier of iodine, as the reaction takes place very slowly without it. (Gantter.) [83] Waller [84] finds that the addition of 50 ml. HCl, specific gravity, 1.19, to the mixed iodine solution preserves it for months. Of the other metallic chlorides, $CoCl_2$ gives the highest true iodine value, $MnCl_2$, $MnBr_2$ and $NiCl_2$ cause practically no addition. (Schweitzer and Lungwitz.) [85]

2. *The Quantity of Iodine Solution Used.* The mixed iodine solution as made up should require about 53 ml. of the thiosulfate. Before using, a rough titration should be made, and if it be much weaker than this, a proportionately larger amount added. The action of a large excess of iodine is to increase the substitution rather than addition; increase in temperature or in time produces the same effect.[86]

The excess of iodine recommended is from 150 to 250%; some observers recommend from 400 [87] to 600%.[88]

3. *Length of Time.* Two hours is sufficient for olive oil, tallow, and lard, while for linseed oil, 18 hours, balsams, and resins 24 hours should be allowed.[89]

Ingle [90] has shown that the free acid formed during the process is due to the action of water upon the iodochlorides. Some of these are reduced by potassium iodide with liberation of iodine and consequent reduction in the iodine absorption. Iodine chloride is the active agent, and not hypoiodous acid.

For the calculation of the percentage of adulteration of one oil by another, Hübl gives the following formula: [91]

" Let x = percentage of one oil and y = percentage of the other oil, further,

[78] J. Soc. Chem. Ind., **2**, 435, 1883.
[79] Dingler Polyt. J., **253**, 281; also J. Soc. Chem. Ind., **3**, 641, 1884.
[80] J. Chem. Ind., **11**, 183, abstr., 1892.
[81] Ibid., **13**, 1100, abstr., 1894.
[82] J. Soc. Chem. Ind., **14**, 130, 1895.
[83] Ibid., **12**, 717, abstr., 1893.
[84] Chem. Ztg., **19**, 1786, 1831, 1895.
[85] J. Soc. Chem. Ind., **14**, 1031, 1895.
[86] J. Soc. Chem. Ind., **12**, 717, abstr., 1893.
[87] Ibid., **14**, 1031, 1895.
[88] Holde, Mitt. kgl. Techn. Versuchs., **9**, 81, 1891.
[89] Dieterich, J. Soc. Chem. Ind., **12**, 381, 1893.
[90] J. Soc. Chem. Ind., **21**, 587, 1902.
[91] Dingler Polyt. J., **253**, 281, 1884.

m = iodine value of pure oil x, n of pure oil y, and I of the sample under examination, then

$$x = \frac{100(I-n)}{m-n}.$$

He further states that the age of the oil, provided it be not rancid or thickened, is without influence on the iodine value. Ballantyne [92] finds that light and air diminish the iodine number.

As might be expected, the iodine value is inversely proportional to the cold test.

The method, as will be seen, is a conventional one, and the best results will be obtained by using measured quantities of reagents and carrying through the process in the same manner every time.[93]

The calculation is perhaps most easily made as follows: Subtract the number of ml. of thiosulfate used for the titration of the oil, from that obtained by titrating the blank—this gives the thiosulfate equivalent to the iodine absorbed by the oil. Multiply this number (of ml.) by the value of the thiosulfate in terms of iodine, and the result is the number of grams of iodine absorbed by the oil; this divided by the weight of oil used and multiplied by 100 gives the iodine number.

In case it be desired to recover the iodine used, reference may be had to an article by Dieterich, abstracted in the Jour. Soc. Chem. Ind., ***15***, 680, 1896.

Oxidized Oils. Iodine Number of.—To find the original iodine number of a semi-drying or non-drying oil which has been altered by atmospheric oxidation, add 0.8 to the iodine number found on the altered sample for each increase of 0.001 in the specific gravity $\left(\text{taken at } \frac{15.5^\circ\text{ C.}}{15.5^\circ\text{ C.}}\right)$ [94].

Bromine Number or Value.—The iodine method just described has, among others, the disadvantage that it fails to distinguish between addition and substitution; this is sometimes of importance, and to accomplish it McIlhiney [95] makes use of the bromine absorption.

Manipulation.—From 0.2 to 0.3 gram of a drying oil, 0.4 to 0.5 of a non-drying oil, or 1.0 to 1.2 grams of a solid fat, are accurately weighed into the 300 ml. bottle, as in the iodine number (page 1767).

The oil is dissolved in 10 ml. of carbon tetrachloride, and 20 ml. of bromine solution (Reagents) added, best from a burette. After allowing it to stand two minutes by the watch, 20 or 30 ml. of potassium iodide are added, in the manner described below, the amount depending upon the excess of bromine. To prevent loss of bromine and hydrobromic acid, a short piece of thin and wide rubber tubing—" bill tie tubing "—is slipped over the lip of the bottle, thus forming a well around the stopper; some of the iodide solution is poured into this and the bottle cooled in cracked ice. Upon removing the stopper the solution is sucked into the bottle, it is shaken to insure the solution of the vapors, and the remainder of the reagent added. The iodine liberated is titrated by sodium thiosulfate in the usual way.

[92] J. Soc. Chem. Ind., **10**, 31, 1891.

[93] If, for example, the water be added before the iodide solution, the iodine number is changed by 0.3 per cent.

[94] Sherman and Falk, J. Am. Chem. Soc., **27**, 608, 1895.

[95] J. Am. Chem. Soc., **21**, 1084, 1899.

When this titration is finished, 5 ml. of the potassium iodate solution are added and the titration repeated. The iodine liberated in this reaction is equivalent to the hydrobromic acid present. Blank determinations should be made with the reagents used, as with the iodine number.

NOTES.—Oftentimes, particularly with resins, emulsification of the solution takes place, masking the end-point. This can be prevented by the addition of 50 or 100 ml. of a 10% solution of salt.

In case ice be not at hand, the vapors will probably be completely absorbed by passing through the iodine solution in the rubber well.

The reactions involved, in addition to those on page 1768, are:

Palmitin

$$(C_{15}H_{31}COO)_5C_3H_5+3Br_2=(C_{15}H_{30}BrCOO)_3C_3H_5+3HBr.$$

$$3HBr+3KI=3KBr+3HI.$$

$$6HI+KIO_3=3I_2+3H_2O+KI.$$

The calculation is similar to that followed in the iodine number (page 1767).

The percentage of bromine found as hydrobromic acid is called the bromine substitution figure, and the total percentage absorbed, less twice the bromine substitution figure, gives the bromine addition figure.

The method has the further advantages that it is rapid, the bromine solution is permanent and inexpensive. For data upon various oils, see table on page 1795.

Saponification Value.—This is expressed by the number of milligrams of potassium hydrate necessary to saponify one gram of the oil. It is called from the originator " Koettstorfer [96] number or value," also " Saponification number," and must not be confounded with " Saponification equivalent " as proposed by Allen,[97] which is the number of grams of oil saponified by 56.1 grams of potassium hydrate.

METHOD [98]

Solutions Required: ***Alcoholic solution for saponification.***—Dissolve 58 grams of potassium hydrate " purified by alcohol " in 500 ml. of 95% purified ethyl alcohol. Allow the solution to settle in a dark place. Draw off the clear solution or filter through an asbestos filter and make up to 1 liter with 95% alcohol. The solution so prepared shall stand at least 20 hours before it is standardized.

Alcohol.—Purify 95% ethyl alcohol with silver oxide in the following manner:[99]

Dissolve 1.5 grams of c.p. silver nitrate in about 3 ml. of water, add to 1 liter of alcohol in a glass-stoppered bottle, and mix thoroughly. Dissolve 3 grams of potassium hydrate (by alcohol) in 10 to 15 ml. of warm alcohol. After cooling, add slowly to the alcoholic silver nitrate solution, stirring slightly. Allow the precipitated silver oxide to settle, siphon off the clear solution, and distil on a steam bath.

Standard hydrochloric acid solution.—One-half normal solution.

[96] Z. anal. Chem., **18**, 199, 1879.
[97] Commercial Organic Analysis, **2**, 40.
[98] Tech. Paper 323B.
[99] Dunlap, J. Am. Chem. Soc., **28**, 397, 1906.

Phenolphthalein solution.—One gram phenolphthalein in 100 ml. alcohol and water.

Apparatus.—The saponification shall be carried out in a wide-mouthed, flat-bottom extraction flask, or Erlenmeyer flask, of 250 to 300 ml. capacity, fitted to a reliable condenser properly connected with a good cork. The boiling shall preferably be carried on by means of an electric hot plate.

Blank Determination.—Determination shall be made in duplicate in the alcoholic potash solution in the following manner:

Measure accurately into the flask 25 ml. of alcoholic potash solution from a calibrated pipette. The tip and outside of the pipette shall be wiped off with a clean filter paper before the solution is delivered, then rinsed out with 25 ml. of neutral alcohol. If a standard burette is used, allow 60 seconds total time for drawing and draining. Connect the flask to a suitable condenser and boil for 3 hours. Before disconnecting the flask, wash out the condenser with a few milliliters of neutral alcohol; if a Soxhlet is used as the condenser, the tip shall be washed off into the flask. Titrate while hot with N/2 HCl, using 3 drops of phenolphthalein as indicator. The total number of milliliters of N/2 HCl required for the blank represents the strength of the alcoholic potash solution.

Procedure.—For straight fats or oils, use 2 or 3 grams of the material, for oils containing over 30% of fatty oils, use about 5 grams, and for oils containing less than 30% of fatty oils, use about 10 grams.

Weigh the oil accurately, by difference, p. 1768, from a small beaker into the saponification flask. Add 25 ml. of alcoholic potash solution and 25 ml. of neutral alcohol in the same manner as for the blank, connect to the condenser, and boil for 3 hours. Titrate while hot. Calculate the saponification number from the difference between the number of milliliters of N/2 HCl required for the determination and the average of the two blanks, using the formula:

$$\text{Saponification number} = \frac{\text{difference, milliliters} \times 28.05}{\text{weight of oil, grams}}.$$

Petrolic ether may be used with compounded cylinder oils in the quantity of 50 ml., providing a Soxhlet extraction flask is used to collect this petrolic ether periodically. The Soxhlet flask should be so adjusted, through the addition of glass rodding or beads when necessary, that it will just overflow with the full quantity of petrolic ether.

The percentage of fatty oil (or fat) in a compounded petroleum product can be calculated from the saponification number of such a product only when the saponification number of the fatty oil is known. If the saponification numbers of both fatty oil and compounded oil are known, the following formula should be used:

$$\text{Percentage of fatty oil} = \frac{100 \times \text{saponification number of compounded oil}}{\text{saponification number of fatty oil}}.$$

For this determination the following values of saponification number may be used:

Fatty Oil	Saponification Number	Fatty Oil	Saponification Number
Lard oil	192–198	Soya bean	189–197
Tallow	193–198	Peanut	186–197
Neat's-foot	193–204	Cottonseed	191–197
Fish	140–193	Blown rapeseed	195–216
Sperm	120–140	Blown cottonseed	210–225
Castor	176–187	Degras	110–210
Rapeseed	170–179		

Notes.—Many prefer to cork the flasks tightly and tie down the stoppers, thus saponifying under pressure; others make use of a return flow condenser, oftentimes merely a long glass tube.

McIlhiney [100] has applied the process to dark-colored substances by making use of the principle that when ammonium chloride is added to a neutral soap solution, and the mixture distilled, the amount of ammonia freed is equivalent to the quantity of alkali combined with the fatty acids. As a description of the process is beyond the scope of the present volume, reference must be had to the original article.

As ordinarily prepared, the alcoholic potash solution turns rapidly reddish brown, so that it is very difficult to note the end-point. This trouble can be partially avoided by adding a drop or two of the solution to the diluted indicator contained upon a tile after the manner of the titration of iron by bichromate. As the color is probably due to the polymerization of the aldehyde formed by the oxidation of the alcohol, it is more satisfactory to use for the preparation of the potash solution an alcohol which is practically aldehyde free. Alcoholic potash made up from this, using the so-called "potash by alcohol," will give a solution which will remain water-white for weeks. "Thymol blue" may be used as an indicator.

The writer has found, if the stock solution be kept under an atmosphere of hydrogen, that the coloration by standing is almost entirely prevented.

This method has also been refined by Gill and Simms, J. Ind. & Eng. Chem., **13**, 547 (1921) so that a single drop, 0.03 gram, suffices for a test.

Detection of Unsaponifiable Oils.—The qualitative detection takes place by observing the behavior of the solution obtained by boiling the oil with alcoholic potash when diluted with warm water. Any unsaponifiable material will manifest itself as oily drops in the clear alcoholic solution, or as a whitish cloud on the addition of water.

The quantitative determination may take place in two ways: 1. From the saponification number. 2. By gravimetric methods.

1. From the Saponification Number.—On pages 1795 and 1796 it will be noticed that, except for castor, rape, and sperm oils, the saponification number averages 193. If the number found be divided by this figure, the percentage of saponifiable matter will be obtained; this subtracted from 100 will give the unsaponifiable matter. This method gives no idea of the kind of saponifiable matter.

2. By Gravimetric Methods.—The procedure is essentially that of Spitz and Hönig: [101] 10 grams of the oil are boiled fifteen minutes under a return-flow condenser with 50 ml. of 5% alcoholic potash; [102] 40 ml. of water are added and the boiling repeated. The liquid is allowed to cool, washed into a separatory funnel with 50% alcohol and 50 ml. of 86° gasoline, thoroughly shaken

[100] J. Am. Chem. Soc., **16**, 409, 1894. For a discussion of the theory of the process, see Lewkowitsch, J. Soc. Chem. Ind., **17**, 1107, 1898.

[101] Z. ang. Chem., **19**, 565, 1891.

[102] The potash is made by dissolving purified potash in the smallest possible quantity of water and adding absolute alcohol.

and allowed to stand. The gasoline layer should separate clearly and quickly from the soap solution and the latter is drawn off; the gasoline is washed 2 or 3 times with 50% alcohol to extract any soap, and these washings added to the soap solution. This latter is extracted, until upon evaporation the gasoline leaves no stain upon paper, care being taken to wash the gasoline extracts each time with 50% alcohol; three extractions with gasoline are usually sufficient.

The gasoline is distilled from these extracts, the residue heated until the gasoline odor disappears, and weighed. From the appearance of the residue some idea of the kind of unsaponifiable matter can be obtained. This in the case of sperm oil will be mainly solid alcohols, probably of the ethylene series.

According to Schicht and Halpern [103] this method is open to the following errors: incomplete saponification, incomplete extraction, solubility of soaps in the solvent, and the solubility of the unsaponifiable matter in the washing solution. Their improved method is as follows: 5 grams of fat [104] with 3 grams of solid caustic potash dissolved in a little water and 25 ml. of absolute alcohol are boiled half an hour under a reflux condenser. After cooling 25 ml. of 10% KCl are added and the solution is then shaken four times with 200 ml. of petroleum ether distilling under 60°. The petroleum ether is evaporated and, without washing, the residue is dissolved in 25 ml. absolute alcohol and the solution made slightly alkaline with normal alkali; 25 ml. of 10% KCl are added and the shaking with petroleum ether repeated. The petroleum ether solution is shaken with 100 ml. of 50% alcohol and the wash solution with 100 ml. petroleum of ether, which is afterwards washed with 100 ml. of 50% alcohol. After combining the extracts the petroleum ether is driven off and the residue dried and weighed.

Note.—Care should be taken to use gasoline which leaves no residue on evaporation at 100° C.

Identification of the Unsaponifiable Matter.—The unsaponifiable matter is either liquid or solid; in case it is liquid, it may be (1) *hydrocarbon oils*, either mineral, or formed by the distillation of waste fats, as wool grease, or (2) *tar oils*, "dead oils," etc., obtained by the distillation of coal tar; or (3) *rosin oils*.

If it be a question of one of these three, the specific gravity will usually decide it; that of the hydrocarbon oils is 0.855 to 0.930, of the rosin oils 0.96 to 0.99, while the tar oils are heavier than water. Rosin oils would be shown by the Liebermann-Storch test, p. 1781; a mixture of mineral and tar oils would be identified by treatment with an equal quantity of nitric acid, sp.gr. 1.45, both previously cooled to 15° C., and noting the rise of temperature. Mineral oils give a very slight rise, being paraffins, while the tar oils belong to the benzole series and are more easily nitrated. Hydrocarbon oils from distilled grease oleins can be identified by their refractive index and rotatory power.[105]

Solid unsaponifiable matters may be:

(4) *Paraffin.*

[103] Chem. Ztg., **31**, 279, 1907.

[104] For linseed and other oils, ten or twenty times this weight should be used, the alkali being correspondingly increased.

[105] Gill and Forrest, J. Am. Chem. Soc., **32**, 1071; Gill and Mason, J. Am. Chem. Soc., **26**, 665.

(5) *Ceresene*—refined ozokerite.

(6) *Higher alcohols* of the paraffin series, as cetyl, $C_{16}H_{33}OH$, coming from the saponification of sperm oil and other waxes.

(7) *Cholesterol*, $C_{26}H_{43}OH$, and its isomers, phytosterol, sitosterol, isocholesterol, etc.

(8) *Lactones*, internal anhydrides of oxy acids as stearlactone,

$$C_{14}H_{29}CHOHCH_2CH_2COOH = C_{14}H_{29}\underbrace{CHCH_2CH_2COO}+H_2O.$$

These may be separated by boiling for two hours with an equal quantity of acetic anhydride; if the substance dissolves and does not precipitate on cooling, higher alcohols are indicated; if a mass of crystals separates out on cooling, cholesterol and its isomers, or a mixture of these with the higher alcohols is indicated; if an oily layer remains on top, it is an indication of the presence of paraffin or ceresene. For the complete separation and identification of these reference must be had to Lewkowitsch, "Analysis of Fats, Oils, and Waxes," as it is beyond the limits of this chapter.

Test for Animal or Vegetable Oils.—Animal oils contain cholesterol, $C_{26}H_{43}OH$, while vegetable oils contain the isomeric body phytosterol; hence the isolation and identification of these compounds enables one to say with certainty as to the presence of one class of oil or the other—for example as to the presence of fish oil in linseed. The quantity of these bodies varies from 0.2 to 1%. The method is essentially that of Bömer.[106] Fifty grams of the oil are boiled in a flask with a return cooler with 75 ml. of 95% alcohol for five minutes and the alcoholic solution separated; this is repeated with another portion of alcohol. The alcoholic solutions are mixed with 15 ml. of 30% sodium hydroxide and evaporated on a water bath nearly to dryness in a porcelain dish and the residue shaken out with ether. The ether is evaporated, the residue taken up with a little ether, filtered, again evaporated, dissolved in 95% alcohol (by volume), and allowed to crystallize slowly. Bömer states that the form of the crystals is more to be relied upon than a determination of their melting-point. Cholesterol crystallizes from alcohol or ether in leaflets or rhomboid tables containing one molecule of water of crystallization. Phytosterol crystallizes also from alcohol with one molecule of water in needles forming stars or bundles. As a further means of identification, some of the esters should be made and their melting-points determined.

To this end the crystals above obtained are heated over a low flame in a small porcelain dish covered with a watch-glass, with 2 or 3 ml. of acetic or other acid anhydride until it boils: the watch-glass is removed and the excess of anhydride evaporated on the water bath. The contents of the dish are treated with a small quantity of absolute alcohol to prevent crystallization, more alcohol added and the solution allowed to crystallize. The crystals are filtered off through a very small filter, washed with a small quantity of 95% alcohol, dissolved in absolute alcohol, and recrystallized until a constant melting-point is obtained.

The following table shows the corrected melting-points of these alcohols and their esters:

[106] J. Soc. Chem. Ind., **17**, 954, 1898; Tolman, J. Am. Chem. Soc., **27**, 590, 1905; Tolman, Bull. 107, U. S. Dept. Agriculture, 1907.

	Cholesterol	Phytosterol
Alcohol	148–150.8°	136–143.8°
Acetate	113–114°	120–137°
Benzoate	135–151°	142–148°
Propionate	97–98°	104–105°

NOTES.—Some directions state, in isolating the cholesterol or phytosterol, to boil with the 30% sodium hydroxide until one-fourth of the alcohol is evaporated. As a result of repeated experiments this has been found to cut down the yield so much that on a large scale practically none of these bodies, particularly phytosterol, was obtained. This agrees with the observation of Lewkowitsch that by heating cholesterol with normal alcoholic potash, cholesterin hydrate is obtained.

The following test will serve to differentiate between cholesterol and phytosterol.[107] A very small quantity of cholesterol is warmed with 1.5 ml. absolute alcohol and a trace of isodulcit or rhamnose (δ-dimethylfurfural) added. After cooling, an equal volume of concentrated sulfuric acid is added, so as to form a layer below the solution, whereupon a raspberry-colored ring is produced at the zone of contact of the two liquids. On mixing the layers while the tube is cooled in a current of cold water, the mixture becomes intensely colored. With phytosterol the reaction fails or at most a pink color. Similar reactions are given by abietic acid. Or mix the pure unsaponifiable matter with an equal quantity of pure cholesterol; if the melting point be unchanged, the unsaponifiable matter is cholesterol; lowering of the melting point indicates phytosterol.

As little as 1% of cotton-seed has been found in lard, and 4% in any oil has been detected by this test.

For the means of distinguishing between drying and marine animal oils, see Halphen, J. Pharm. Chim., **14**, 391 (1901), abstracted J. Soc. Chem. Ind., **21**, 74, or Chem. Centralb., **72**, ii, 1097 and 1323.

Tests for Antifluorescents.[108]—It is often desired to remove the fluorescence or "bloom" from petroleum oils. This may be effected by refining with chromic acid, or more easily by the addition of a small quantity of nitronaphthalene or nitro-benzene. The latter may often be detected by the odor.

The test is made by boiling about 1 ml. of the oil with 3 ml. of 10% alcoholic potash for one to two minutes. If either of the nitro compounds be present, a blood- or violet-red coloration is produced; a pure mineral oil is changed only to yellow or brownish-yellow by this treatment. In case the characteristic color does not appear the following test may be applied.[109] It depends upon the reduction of the nitro bodies to their amines.

A few ml. of the oil are heated with feathered tin and hydrochloric acid in an Erlenmeyer flask for ten minutes: this can be aided by the introduction of a piece of platinum wire. The oil is separated by a separatory funnel and filtration through a wet filter, the filtrate treated in another separatory with sodium hydrate until the tin hydrate redissolves and shaken out with 10–20 ml. of ether. The amines go into solution in the ether, giving to it a violet color and fluorescence in the case of α-naphthylamine. These can be recognized by their odor, that of naphthylamine being very characteristic. The latter may be recognized by dissolving in hydrochloric acid, evaporating the latter, and upon treatment with ferric chloride obtaining an azure-blue precipitate. This changes when filtered off to purple-red and the filtrate to violet.

Aniline can be recognized by solution in concentrated sulfuric acid and the red and then blue color which appears on the addition of a small crystal of

[107] Neuberg and Rauchwerger, abstr. J. Soc. Chem. Ind., **23**, 1163, 1904.
[108] Holde, J. Soc. Chem. Ind., **13**, 906, 1893.
[109] Holde, "Examination of Hydrocarbon Oils," p. 75.

potassium bichromate. Free aniline is also temporarily colored violet by a solution of bleaching powder.

Acetyl Value.—The estimation of the acetyl value is seldom required in oil analysis, it being characteristic only when triglycerides are present. For a description of the method and its applications, reference must be had to the larger works, as Lewkowitsch or Allen.

Special Tests for Certain Oils

Lewkowitsch says:[110] "It should be distinctly understood that color reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can only be used as a preliminary test, or as a confirmatory test. The ease with which this test can be carried out, and its apparent reliability, have led to an over-estimation of this very useful and important reaction; so much so, that grave errors may be committed by those who assign to this test an exclusive or even a paramount importance. It is altogether unjustifiable to look upon this test, as has been done, as permitting of quantitative interpretation."

Bechi's Test for Cotton-seed Oil.—This depends upon the supposition that a substance of an aldehydic nature which reduces silver nitrate is contained in the oil. The method is essentially that of Milliau.[111]

Fifteen grams of oil are weighed into a No. 6 porcelain dish, using the coarse scales, and heated for about ten minutes upon the water bath; a mixture of 10 ml. of 30% caustic soda and 10 ml. of the alcohol is slowly poured upon the oil. The whole is occasionally stirred until the mass becomes clear and homogeneous, and 150 ml. of hot distilled water slowly added so as not to decompose the soap, and the boiling continued until the alcohol is expelled. Dilute sulfuric acid (1 : 10) is added to acid reaction, and the separated fatty acids washed three times by decantation with cold water. A portion of these is brought into a large test-tube, 15 ml. of alcohol and 2 ml. of 3% silver nitrate solution are added, the tube is wrapped with brown paper, held in place by an elastic band, and heated, with constant stirring, in the water bath until one-third of the alcohol is expelled, which is replaced by 10 ml. of water. This heating is continued for a few minutes longer and the coloration of the insoluble fatty acids observed. The presence of cotton-seed oil in any appreciable proportion causes a mirrorlike precipitate of metallic silver, which blackens the fatty acids of the mixture.

Notes.—The alcohol should be proved free from aldehyde by a blank test. Unless the mixture in the test-tube be thoroughly stirred while heating, it will "bump" and eject the contents. Other methods of procedure consist in applying the test to the oil itself, often after treatment with dilute caustic soda and nitric acid. (Wesson.[112]) The writer had a case in which the *oil* gave the test while the *fatty acids* gave no blackening, showing there was something in the oil itself other than cotton-seed oil which reduced the silver nitrate. Students have no difficulty in detecting a 5% adulteration with cotton-seed oil.

Dupont[113] thinks that the reduction of silver nitrate is due rather to sulfur com-

[110] "Chemical Technology and Analysis of Fats, Oils and Waxes," **2**, 203.

[111] J. Am. Chem. Soc., **15**, 164, 1893.

[112] J. Am. Chem. Soc., **17**, 723, 1895.

[113] Bull. Soc. Chem. (3), **13**, 696; J. Soc. Chem. Ind., **14**, 811, 1895; also Charabot and March, Bull. Soc. Chim., **21**, 252, 1899.

pounds contained in the oil; by passing steam over the oil he obtained a product containing sulfur and the oil still gave the Bechi test. This work has been repeated and confirmed by the author.[114] It is to be noted that while the fatty acids blacken silver nitrate they do not color cadmium, lead, or copper salts, but reduce mercury compounds. No indication of an aldehyde was noted by the fuchsine or ammonia tests. The supposition that the reducing substance is aldehydic in its nature finds support in the fact that if the oil be heated to 240° [115] or be kept for some time [116] it loses this peculiar property.

By purifying the acids by the lead salts Tortelli and Ruggeri [117] are able to detect as little as 10% of heated cotton-seed oil.

It is to be noted that pure lard, tung and olive oil are not infrequently met with which give the test, consequently its indications cannot be considered as conclusive.

Halphen's Test for Cotton-seed Oil.[118]—This depends upon the observation that this oil contains an unsaturated fatty acid which combines with sulfur, giving a colored compound.[119]

Procedure.—Ten ml. of the oil or melted fat are heated, in a large test-tube with a long glass condenser tube attached, with an equal volume of amyl alcohol and of carbon bisulfide solution of sulfur (Reagents), at first with frequent agitation, in a steam bath, and then, after the violent boiling has ceased, in a brine bath (105–110° C.) for forty-five minutes to three hours, according to the quantity of adulterant present, the tube being occasionally removed and shaken. As little as 1% will give a crimson wine coloration in twenty minutes.[120]

Notes.—If the mixture be heated for too long a time a misleading brownish-red color due to burning is produced. The reaction seems to be peculiar to this oil; it is more sensitive with fresh than old fats, and while, by comparison with a blank, $\frac{1}{16}$ of 1% is noticeable, ¼ of 1% is easily detected. Cotton-seed oil which has been heated to 250° C. does not give the test; the oil is then not available as food. Heating to 200° C. does not interfere with the test.[121]

The test is not given by an oil which has been oxidized with sulfuric acid and potassium permanganate, although such an oil gives the Bechi test.[122] This shows that the two tests are not produced by the same substance. Nor is this test or that of Bechi given by an oil which has been treated with chlorine or sulfurous acid.[123] If treated with the former it is no longer edible; an oil treated with sulfurous acid and washed with alcohol cannot be distinguished from ordinary cotton-seed oil and does not, as already stated, respond to either the Halphen or Bechi test. In this case the test for phytosterol is the only means of determining if it has been added to an animal oil. The test is also given by kapok oil, which is used as an edible oil in China, the East and West Indies, and in Africa; baobab oil also gives it.

Lard from hogs fed on cotton-seed meal shows this reaction strongly, as if it were 25% oil.[124] The butter from cows similarly fed also yields the reaction.[125]

[114] Gill and Dennison, J. Am. Chem. Soc., **24**, 397, 1902.
[115] Holde, J. Soc. Chem. Ind., **11**, 637, 1892.
[116] Wilson, Chem. News, **59**, 99, 1889.
[117] J. Soc. Chem. Ind., **20**, 753, 1901.
[118] Halphen, J. Pharm. Chim., 390, 1897.
[119] Raikow, Chem. Ztg., **24**, 562, 583, 1900.
[120] Oilar, Am. Chem. J., **24**, 355; abstr. Anal., **26**, 22, 1901.
[121] Fischer and Peyan, Analyst, **30**, 131, 1905; Soltsien, Z. öffentl. Chem., **5**, 135, 1899; J. Soc. Chem. Ind., **18**, 865.
[122] Raikow, loc. cit.
[123] Petkow, Analyst, **32**, 123, 1907.
[124] Soltsien, Z. öffentl. Chem., **7**, 140, 1901.
[125] Wauters, J. Soc. Chem. Ind., **19**, 172, 1900.

The test may be applied to the soaps or fatty acids, provided they are not too deeply colored.

The amyl alcohol cannot be omitted nor substituted by ethyl alcohol without impairing the delicacy of the test.[126] The compound in the oil cannot be removed by treating with animal charcoal.[124]

Hexabromide Test for Linseed Oil.—The object of the test is to determine the amount of insoluble bromides of the fatty acids contained in the oil. Linseed gives the highest percentage of bromides of any of the common oils, consequently its adulteration can be shown by the hexabromides.

Fifteen grams of the oil are saponified by boiling with 15 ml. of potassium hydroxide solution, sp.gr., 1.35, and 15 ml. of alcohol in a flask under a reflux condenser; 300 ml. of warm water are added and the solution distilled with steam until the alcohol is removed. Dilute sulfuric acid is added to excess, the solution heated until the fatty acids are obtained as a clear oily upper layer; this is washed several times with hot distilled water until free from sulfuric acid, using methyl orange as an indicator. This does not react with fatty acids of low molecular weight which being soluble in water may redden litmus. This washing is effected in an atmosphere of inert gas, carbonic acid or hydrogen by stopping the flask with a three-holed stopper, carrying a siphon, an entrance and an exit tube for the gas. The acids are siphoned into a small Erlenmeyer flask and in case a few drops of water come over—an equal quantity of alcohol added and dried upon the water bath in a stream of dry inert gas.

In order to test for the presence of unsaponified fat, 3 ml. are dissolved in 15 ml. of 95% (by volume) alcohol, and 15 ml. of aqueous ammonia are added. If an appreciable amount of fat has escaped saponification, the mixture will become turbid (Geitel).

Two grams of mixed fatty acids[128] are dissolved in a flask in 27 ml. of dry ether, cooled down to 10° C., and 0.25 ml. of bromine allowed to run into the solution from a very finely-drawn-out pipette, the time allowed for this being about twenty minutes. The remaining 0.25 ml. of bromine is added somewhat more rapidly, within about ten minutes, the bromination thus occupying about thirty minutes. The authors attach great value to the exact observance of the time. The temperature should never be allowed to rise during bromination above 5°. The flask is corked and allowed to stand for two hours at 0°. The ethereal solution is next decanted through a weighed asbestos or paper filter (Lewkowitsch) and the precipitate is washed with five lots of 5 ml. each of dried and cooled ether. After complete draining, the precipitate is dried for two hours at 80° to 85°, and allowed to cool in a desiccator. The temperature is designedly kept below 100°, as the authors found that the color of the hexabromide becomes somewhat gray if the drying takes place at 100°. The melting-point of the hexabromides was 177°, whereas the melting-point of pure hexabromide has been found to be higher. No doubt the low melting-point is due to the drying having been carried out below 100°.

Nevertheless small traces of retained moisture cannot account for the much larger yield of hexabromide which the authors obtained.

The yields of hexabromide obtained by these authors are as follows:

[126] Soltsien, loc. cit., **25**, Oilar, loc. cit.
[127] Utz, Rev. Fett u. Harz. Ind., **9**, 125, 1902.
[128] Eibner and Muggenthaler, Farben Ztg., 1912.

Fatty Acids	Per cent	Fatty Acids	Per cent
Perilla oil	64.12	Tung oil	nil
Linseed oil, Baltic	57.96	Soya bean oil	up to 7.78
Linseed oil, Dutch	51.73	Poppy seed oil	nil
Linseed oil, La Plata	51.66	Rape oil	6.34
Linseed oil, Indian	50.50		

Bailey and Baldsiefen, J. I. and E. Chem., **12**, 1189 (1920), have devised a modification which is more elaborate and may give more accurate results.

Bellier's Qualitative Test for Peanut Oil.[129]

The necessary reagents are:

Alcoholic potash, made by dissolving 8.5 grams of pure potassium hydroxide in 70 per cent alcohol and making up to 100 ml.

Acetic acid of such strength that 1.5 ml. will neutralize 5 ml. of the alcoholic potash. (Acid having a specific gravity of 1.04 is approximately correct.)

Procedure.—Weigh 1 gram of the oil into a dry test-tube, add 5 ml. of the alcoholic potash and boil gently over a small flame, avoiding evaporation as much as possible. Boil until the oil is completely saponified, which will take a little over 2 minutes. Add 1.5 ml. of acetic acid, or just sufficient to neutralize the alcoholic potash (use phenolphthalein as an indicator), mix well, cool rapidly by placing the test-tube in water at 17° to 19° C. and leave in the water at the stated temperature for not less than 30 minutes, shaking occasionally. Then add 50 ml. of 70 per cent alcohol containing 1 per cent by volume of hydrochloric acid (sp.gr. 1.16), shake well and again place in water at 17° to 19° for an hour. If no peanut oil be present, the liquid will remain clear or at most slightly opalescent; with 10 per cent, or more, of peanut oil a flocculent, crystalline precipitate forms.

Renard [130]-Tolman [131] Quantitative Test.

Weigh 20 grams of oil into an Erlenmeyer flask. Saponify with alcoholic potash, neutralize exactly with dilute acetic acid, using phenolphthalein as indicator, and wash into a 500-ml. flask containing a boiling mixture of 100 ml. of water and 120 ml. of a 20% lead acetate solution. Boil for a minute and then cool the precipitated soap by immersing the flask in water, occasionally giving it a whirling motion to cause the soap to stick to the sides of the flask. After the flask has cooled, the water and excess of lead can be poured off and the soap washed with cold water and with 99% (by volume) alcohol. Add 200 ml. of ether, cork, and allow to stand for some time until the soap is disintegrated, heat on the water bath, using a reflux condenser, and boil for about five minutes. In the oils most of the soap will be dissolved, while in lards, which contain much stearin, part will be left undissolved. Cool the ether solution of soap to 15° or 17° C. and let it stand until all the insoluble soaps have crystallized out (about twelve hours).

Filter and thoroughly wash the precipitate with ether. Wash the soaps on the filter back into the flask by means of a stream of hot water acidified with

[129] The test is not thoroughly dependable.

[130] Renard, Compt. rend., **73**, 1330, 1871; also Archbutt, J. Soc. Chem. Ind., **17**, 1124.

[131] Bull. 107, U. S. Dept. Agriculture, 1907, p. 145.

hydrochloric acid. Add an excess of dilute hydrochloric acid, partially fill the flask with hot water, and heat until the fatty acids form a clear oily layer. Fill the flask with hot water, allow the fatty acids to harden and separate from the precipitated lead chloride, wash, drain, repeat washing with hot water, and dissolve the fatty acids in 100 ml. of boiling 90 per cent (by volume) alcohol. Cool to 15° C., shaking thoroughly to aid crystallization.

From 5 to 10 per cent of peanut oil can be detected by this method, as it effects a complete separation of the soluble acids from the insoluble, which interfere with the crystallization of the arachidic acid. Filter, wash the precipitate twice with 10 ml. of 90% (by volume) alcohol, and then with alcohol 70% (by volume). Dissolve off the filter with boiling absolute alcohol, evaporate to dryness in a weighed dish, dry and weigh. Add to this weight 0.0025 gram for each 10 ml. of 90% alcohol used in the crystallization and washing if done at 15° C.; if done at 20° add 0.0045 gram for each 10 ml. The melting-point of arachidic acid thus obtained is between 71° and 72° C. Twenty times the weight of arachidic acid will give the approximate amount of peanut oil present. No examination for adulterants in olive oil is complete without making the test for peanut oil. Arachidic acid has a characteristic structure and can be detected by the microscope.

Bach's Test for Rapeseed Oil.—According to O. Bach,[132] the acids obtained from rapeseed oil are completely insoluble in David's alcoholic acetic acid, in the proportion of 1 to 15, by volume; those from cottonseed, peanut, sesame, and sunflower oil dissolve on heating. Those from the last oil separate as a granular precipitate at 15°, while from the other three they gelatinize. The acids from olive oil are completely soluble at the ordinary temperature. David's acid is made by mixing 22 ml. of 50% acetic acid (by volume) with 30 ml. of alcohol, sp.gr. 0.817, 92.07% (by weight).

NOTE.—The author has found that Bach's observation cannot be implicitly relied upon, as some rapeseed oils yield acids which are soluble in David's mixture.

Liebermann-Storch Test for Rosin Oil.—One or 2 ml. of the oil are shaken with an equal quantity of acetic anhydride and gently warmed. When cool the acetic anhydride is pipetted off and tested by the addition of 1 drop of concentrated sulfuric acid. A fine violet color is produced in the presence of rosin oil. Tung oil and also cholesterol, which is contained in the animal fats, produce a similar coloration; the latter can be removed by saponifying the oil as completely as possible and shaking out the somewhat dilute soap solution with ether or petroleum ether. The soap solution is then acidified, setting free the fatty acids, and these treated with acetic anhydride as if they were the oil.

Baudouin's, or Camoin's Test for Sesame Oil.[133]

Dissolve 0.1 gram of finely powdered sugar in 10 ml. of hydrochloric acid (sp.gr. 1.18), add 10 ml. of the oil to be tested, shake thoroughly for 1 minute and allow to stand for 10 minutes. In the presence of even a very small admixture of sesame oil, the aqueous solution is colored crimson. It should be observed that some olive oils, especially those of African or Spanish origin, give pink or crimson colors which can be readily differentiated from that due to sesame oil by applying the following modification of the Villavecchia method.

[132] Allen, "Commercial Organic Analysis," 2, pt. 1, 128, 1899.
[133] Official.

Villavecchia Test [134]

Add 2 ml. of furfural to 100 ml. of 95 per cent alcohol by volume and mix thoroughly 0.1 ml. of this solution with 10 ml. of hydrochloric acid (sp.gr. 1.18) and 10 ml. of the oil to be tested by shaking them together for ¼ of a minute. Allow the mixture to stand 10 minutes, observe the color, add 10 ml. of water, shake and again observe the color.

The furfurol may be replaced by 0.1 g. of sugar in 10 ml. HCl, sp.gr. 1.18, and twice the quantity of oil used.

Milliau [135] saponifies as in the Bechi test and dries the acids at 105° and tests them instead of the oil. Lewkowitsch [136] states that this is a needless complication. Da Silva [137] states that this test has given colors with certain Portuguese olive oils; also those of Bari, Brindisi and Lecce. Kreis [138] states that the active or color-giving constituent is probably phenolic in its nature. The reaction is given by other substances,[139] as vanillin, oil of cloves, and cinnamon; this should be borne in mind in testing oils which have been extracted from confectionery. Rancid fats prevent the coloration; it can, however, be brought about even in rancid fats by the addition of an equal quantity of cotton-seed oil.[140]

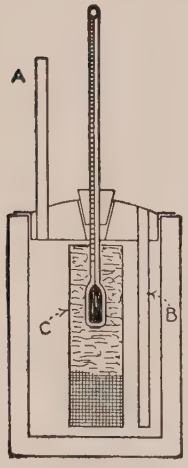


Fig. 257. Mackey's Apparatus.

Free Acid Test.[141]—About 10 grams of oil are weighed (to centigrams) into a 250-ml. Erlenmeyer flask, 60 ml. of neutral alcohol (Reagents) added, the mixture warmed to the boiling point, shaken thoroughly, and titrated with N/6 potassium hydrate, using phenolphthalein, the flask being frequently and thoroughly shaken. The result is conventionally reported in per cent of oleic acid; 1.0 ml. N/6 KOH is equivalent to 0.047 gram oleic acid. Or it can be reported like the saponification number, in milligrams of KOH per gram of oil. For mineral oils use alcohol diluted with its own volume of water.

Spontaneous Combustion Test. Mackey's Apparatus.—The apparatus,[142] Fig. 257, consists of cylindrical copper water bath 7 in. high and 4 in. in diameter (inside measurements), surrounded with a ½-in. water-jacket. The cover is packed with asbestos and carries the draft tubes *A* and *B*, ½ in. in diameter and 6 in. long, which cause a current of air to be sucked down *B* and up *A*, thus ensuring a circulation of air in the apparatus: *C* is a cylinder made of 24-mesh wire gauze 6 in. high and 1½ in. in diameter and supported upon a projection from the bottom of the bath. A thermometer projects down into the center of the cylinder; if a metal condenser be con-

[134] Ibid., 1893, 505; abstr. Analyst, **19**, 47.
[135] J. Am. Chem. Soc., **15**, 162, 1893.
[136] "Oils, Fats and Waxes."
[137] J. Soc. Chem. Ind., **17**, 275, 1898.
[138] Chem. Ztg., **27**, 316, 1903.
[139] Gerber, Analyst, **32**, 90, 1907.
[140] Lauff and Hinsmann, Chem. Ztg., **31**, 1023, 1908.
[141] Tech. Paper 323A.
[142] Mackey, J. Soc. Chem. Ind., **15**, 90, 1896; Gill, ibid., **26**, 185, 1907.

nected to the water bath it can be used indefinitely without refilling and without danger of burning out.

Seven grams of ordinary bleached cotton wadding or " absorbent cotton " are weighed out in a porcelain dish or on a watch-glass, and 14 grams of the oil to be tested poured upon the cotton and thoroughly worked into it, care being taken to replace any oil that is lost. The cotton is then placed in the cylinder, packed about the thermometer so that it occupies the upper 4¼ in. of the cylinder, and put into the boiling water bath. After the expiration of an hour, the bath having been kept in active ebullition, the temperature is read. Any oil which shows a temperature exceeding 100° C. in one hour, or 200° C. in two hours, should be regarded as a dangerous oil, or liable to produce spontaneous combustion. The following tables show the results obtained in using this apparatus.[143]

Oil	Temperature ° C. in		
	1 hr.	1¼ hrs.	1½ hrs.
Olive (neutral)	97–98	100	101
Cotton-seed	112–128	177–242	194–282
Elaine	98–103	101–115	102–191
Olive fatty acids	102–114	—	196

Other values obtained were :

Oil	Temp. ° C.	Time, Minutes	Iodine, No.	Free Acid, per cent
Olive	234	130	85.4	5.3
Lard	234	75	75.2	Trace
Oleic acid	158	188	60.5	—
Cotton-seed	234	70	108.9	Neutral
Linseed	234	65	168.1	Neutral
25° Paraffin	97	135	16.2	—

Besides being used for testing oils it can be applied to testing other materials, oily waste, sawdust, or any mixtures suspected of causing spontaneous combustion.

" The results [144] of the greatest practical value obtained in the use of this apparatus have been, first, determining the cause of fires; and, second, determining the degree of safety of the various oils used in manufacturing. Mineral oil, as is well known, is not liable to spontaneous combustion; and a certain percentage of animal or vegetable oil may be added to mineral oil without materially increasing the danger under ordinary circumstances. This percentage varies according to the oil; with neat's-foot and first quality lard oil some 50 to 60% may be used, with cotton-seed not over 25% is allowable. The

[143] Small percentages (0.5–2.0) of iron, sodium, magnesium or zinc salts in "red" or olive oil may cause a degree of heating which may be dangerous. Gill, Ind. and Eng. Chem., **16**, 23, 1924.

[144] Richards, Tech. Quarterly, **4**, 346, 1891.

claim so often made for so-called ' safe ' oils, said to have been changed by special and secret processes of refining so as to be no longer dangerous, is easily exposed by this test."

Drying Test Upon Glass.[142]—A few drops of oil are brought upon a glass plate inclined at about 30° from the horizontal. A test of the oil is made from time to time by touching it with the fingers, the time at which it does not soil them being noted as the point when it is dry. Good oil should dry in three days.

Archbutt [146] makes this test as follows: A piece of polished plate-glass 7 cm. square by 4 mm. thick is cleaned and counterpoised on the balance; it is then heated for an hour at 200° C. in an air bath to thoroughly dry it. It is taken out, laid on a non-conductor, allowed to cool for three or four minutes, and the hot glass thinly painted with the oil to be tested by means of a camel's-hair brush. When the glass is cold it is weighed and sufficient oil added to make it up to 0.1 gram. Two glasses are coated with the sample and two with a standard oil, all placed on a level surface in a large air bath at 50° C. and heated for nine hours; one set of plates is withdrawn, cooled, and tested by the finger. Good raw linseed is tacky, when tested by the finger when cold, in nine hours and dry in twelve; corn oil is practically dry in fifteen hours, though slightly tacky; cottonseed, partially dry in eighteen hours and fully dry in twenty-one. Refined rape oil dried in forty-eight hours, and olive oil was sticky after thirteen days.

Titer Test.—Under this rather misleading title is expressed the solidification point of the fatty acids derived from a fat or oil; it has nothing at all to do with titration, as might be expected. The test is extensively used for the evaluation of fats, and according to the method provisionally adopted by the Association of Official Agricultural Chemists is carried out as follows: [147]

(*a*) *Standard Thermometer.* The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about 15 in. over all. The thermometer is annealed for 75 hours at 450° C., and the bulb is of Jena normal 16''' glass, moderately thin, so that the thermometer will be quick acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation to be clear-cut and distinct, but quite fine.

(*b*) *Determination.* Saponify 75 grams of fat in a metal dish with 60 ml. of 30% sodium hydroxide (36° Baumé) and 75 ml. of 95% (by volume) alcohol or 120 ml. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used, boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 ml. of 30% sulfuric acid (25° Baumé) to free the fatty acids, and boil until they form a clear, transparent layer. Wash with boiling water until free from sulfuric acid, collect in a small beaker, and place on the steam

[145] Amsel, J. Soc. Chem. Ind., **15**, 222, 1896.
[146] Id., **18**, 347, 1899.
[147] U. S. Dept. of Agriculture, Bureau of Chemistry Bulletin No. 107, p. 135, 1907.

bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using the hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15 or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 by 4 in.) and made of glass about 1 mm. in thickness. Place in a 16-oz. salt-mouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 by 6 in.), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.1° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 ml. in a test-tube and add 15 ml. of alcohol (95% by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp.gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

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Hefter, G. Technologie der Fette, Oele, und Wachsarten des Pflanzen und Tierreichs. 4 volumes, 1906.

Ubbelohde, L. Chemie, Analyse und Gewinnung der Oele, Fette und Wachse. 4 volumes, 1908.

EDIBLE FATS

These include butter, lard and hardened oils.

Butter is examined for water, fat, ash, curd, and salt; these are usually present in the following proportions:

	Per cent	Average per cent
Fat	78 –90	82
Water	5 –20	12
Salt	0.4–15	5
Curd	0.1– 5	1

These are determined as follows: weigh about 2 grams of butter into a platinum Gooch crucible half filled with ignited fibrous asbestos, and dry it at 100° C. to constant weight. The loss is the amount of ***water.*** Dissolve out

the fat by repeated treatment with petroleum ether and again dry to constant weight. The loss represents the amount of ***fat.*** Ignite the crucible with a low flame or in a muffle, being careful not to volatilize the salt, until a light-gray ash is obtained. The loss represents ***curd*** and the residue ***ash.*** By extraction of the ash with water, and neutralization with calcium carbonate, the salt can be titrated with silver nitrate.

Examination of the Fat.—Butter is adulterated with oleomargarine, renovated butter, and cocoanut oil. The first may be detected by testing for cottonseed or sesame oil either by the color tests or by the index of refraction; this at 25° is for butter 1.459–1.462, for oleo. 1.465–1.470. Owing to the fact that butter contains a large per cent of volatile fatty acids (butyric, caproic, caprylic and capric acids, in all about 8%), adulterants may be detected by determining the amount of these. The process usually employed is that of Reichert modified by Meissl.

Five grams of the clear fat, filtered through absorbent cotton, are weighed into a 250-ml. round-bottomed flask and saponified by 2 ml. potassium hydroxide 1 : 1 and 10 ml. of 95% alcohol, under a return flow condenser for twenty-five minutes. The alcohol is rapidly evaporated off on the water bath until no odor of alcohol is perceptible. Add slowly 160 ml. of recently boiled distilled water which has been cooled to 50° or 60°; warm the flask until a clear solution of the soap is obtained. Cool to about 60° and add 8 ml. sulfuric acid 1 : 4 to liberate the fatty acids. Drop into the flask two bits of pumice (about the size of peas) which have been heated and quenched in water, and tie in a well-fitting cork; warm the flask until the fatty acids have melted and are floating on the liquid. Cool to about 60° and attach the flask to a condenser, using a trap to prevent the sulfuric acid from being mechanically carried over; 110 ml. are distilled into a graduated flask in as nearly thirty minutes as possible. Thoroughly mix the distillate, pour through a dry filter, and titrate 100 ml. with N/10 NaOH, using phenolphthalein as an indicator. Multiply the ml. of alkali by 1.1 and calculate them to 5 grams of fat. The Reichert-Meissl value for butter is from 24 to 34, the average is about 28.8; cocoanut oil gives 6–8 and other fats less than 1.

The procedure is a conventional one and should be followed as exactly as possible. Cocoanut and other vegetable oils would be shown by the fact that the unsaponifiable matter would contain phytosterol; also by the Polenske number.[148] Renovated butter is best shown by the " Spoon or Foam Test." This consists in melting a third of a teaspoonful of the sample in a tablespoon over a small flame and stirring with a match. Increase the heat until the fat boils briskly, stirring thoroughly several times. Oleomargarine and renovated butter boil noisily, sputtering like a mixture of grease and water and produce no foam. Butter boils with less noise and much foam sometimes rising over the sides of the spoon. The pieces of curd in butter are much smaller than in either of the others.

Preservatives, benzoic, boric and salicylic acids, may be examined according to the procedure given in Woodman and Norton, " Air, Water and Food," pp. 154 and 196.

[148] Z. Nahr. Genussm., 7, 193, 1904, also Gill, "Oil Analysis."

Color may be detected according to Allen, " Commercial Organic Analysis," 4th Ed., Vol. II, or Leach's " Food Analysis."

Lard is adulterated with water, 25% being added in some cases, with cottonseed oil or stearine and beef stearine.

Water is determined as with butter; ***cottonseed oil*** or stearine by the usual tests. It should be borne in mind, however, that hogs fed on cottonseed meal yield a lard which will give the Halphen test as strongly as if it contained 25% of the oil. The iodine number and the presence of phytosterol will confirm this test; the iodine number varies widely according to the source of the fat, but in general it may be said it should be between 46 and 66.

Beef stearine is very difficult if not impossible of detection. For this, reference may be had to Lewkowitsch, 5th Ed., Vol. II.

HARDENED OILS

As the name denotes, these are oils which have been changed to more or less solid fats by the addition of hydrogen, in the presence of a catalyst, usually a compound of nickel. This betrays their presence and may be tested for as follows: [149]

Ten grams of the fat are heated on the water bath with 10 ml. of hydrochloric acid (sp.gr. 1.12) with frequent shaking for two or three hours. The fat is removed by filtering through a wet filter, receiving the filtrate in a porcelain dish; after partial evaporation of the filtrate 2 or 3 ml. of concentrated nitric acid are added and the evaporation continued to dryness to ensure the destruction of the organic matter. The residue is dissolved in a few ml. of distilled water, a few drops of a 1% solution of dimethylglyoxime in alcohol added, and a few drops of dilute ammonia. The presence of nickel is shown by the appearance of the red-colored nickel dimethylglyoxime. The amount of nickel can be determined colorimetrically by comparison with solutions containing known quantities.

The quantity of nickel is very minute, not as much as the fats take up when cooked in nickel or nickeled dishes, and need cause no apprehension.

Hydrogenation destroys all the characteristics, particularly the color tests, by which the different oils may be sometimes detected.

[149] Kerr, J. Ind. and Eng. Chem., 6, 207, 1914.

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WAXES

These, as will be remembered, contain no glycerine; the tests applied to them are the same as to the oils. The characteristics of the more commonly occurring waxes are given in the table, p. 1797; sperm oil, which is really a liquid wax, is included among the oils.

MISCELLANEOUS OILS AND LUBRICANTS

PROPERTIES OF SOME OF THE MINERAL OILS

Oil	Specific Gravity, Deg. Baumé at 60° F.	Flash Point, ° F.	Viscosity (Saybolt), at 70° F.	Cold Test, Deg. Fahr.
Black	29	325	100–120	5–15
Ice machine	26–27	325–360	60–100	0–4
Crank case	26–27	455	100	—
Transformer	—	340–380	400	25
Turbine	30	420	160	—
Spindle	30–35	320–390	58–156	—
Loom	28	360	203	—
Engine	27–30	410	190–210	—
Cylinder	23–25	525	200–300*	—
Cylinder	26–28	400–575	—	—

* At 212° F.

Belt Dressings are (1) mixtures of fats, waxes, degras or tallow with castor or fatty oils; (2) vulcanized corn or cottonseed oil thinned with naphtha; (3) preparations containing wood tar; or (4) preparations containing rosin, which is undesirable. Black oils, car oils, well oil or reduced oils are crude oils from which the naphthas and burning oils have been separated by distillation. Crank-case oils are pure mineral oils which emulsify but little with water. Milling-machine or soluble oils are lard, sulfonated oils or mineral oils held in suspension in water by soaps or alkalies, as borax or soda; the soaps used are either ammonium, sodium or potassium with resin, oleic or sulfofatty acids. Rosin oils are obtained by distilling or " running " rosin, each distillate being called a " run " and numbered according to the times it has been distilled. They oxidize quite rapidly and should not be used as lubricants except as soaps in lubricating greases. Screw-cutting oils are often mixtures of 27° Bé. paraffin and 25% fatty oil, preferably cottonseed, although lard oil was formerly used. Stainless oils are spindle or loom oils mixed with fatty oils—lard or neatsfoot. Transformer oils should be either pure mineral or rosin oils and as free as

possible from water, acid, alkali and sulfur. Turbine oils should be of excellent quality, free from acid and tendency to resinify, and low in sulfur. Watch oil is obtained from the porpoise, dolphin, or blackfish, where it exists in cavities in the jaw and in the brain or " melon " of the fish. Lubricating greases are mixtures of soaps of palm oil, tallow or rosin oil (with lime or soda as bases) with various oils or fats such as rosin, tallow or mineral oil. The best are those made from tallow by saponification with caustic soda. They may also contain finely powdered talc or graphite. Non-fluid oils are oils or their greases stiffened with " oil pulp " or " dope," i.e., aluminum oleate or palmitate.

The source, preparation and uses of the various oils and greases are described in Rogers and Aubert's Industrial Chemistry, Chapters XXII, XXIV, XXV and XXVII.

For the guidance of the analyst, the characteristics of the more frequently occurring oils are given, the usual figures being given in italic.

The animal and vegetable oils may be classified into

Drying.—Linseed, Chinese wood, poppyseed, sunflower and menhaden.

Semi-drying.—Corn, cottonseed, sesame, rape, black mustard and horse.

Non-drying.—Castor, almond, peanut, olive, cocoanut, palm, seal, cod-liver, elaine, lard, neatsfoot, tallow, sperm and whale.

REFERENCES

Lewkowitsch, "Technology and Analysis of Oils, Fats and Waxes." 3 vols.
Gill, "A Short Handbook of Oil Analysis."
Battle, "Industrial Oil Engineering."
Lockhart, "American Lubricants."

United States Government Specifications for Petroleum Products

SPECIFICATIONS FOR LUBRICANTS AND LIQUID FUELS. REVISED MARCH 18, 1924

Gasoline

Name and grade	Color, darkest allowed	Doctor test	Corrosion test	Distillation range																Recovery, minimum	Distillation loss, maximum	Acidity test	Sulphur, maximum	Special tests and requirements
				First drop, maximum		5 per cent minimum		5 per cent maximum		20 per cent maximum		50 per cent maximum		90 per cent maximum		96 per cent maximum		End point, maximum						
	Saybolt No.			° *C*	° *F.*	° *C.*	° *F.*	° *C.*	° *F.*	° *C.*	° *F.*	° *C.*	° *F.*	° *C.*	° *F*	° *C.*	° *F*	° *C*	° *F.*	*P. ct.*	*P. ct.*			
Aviation gasoline:																								
Fighting	25	Required	Required	....	....	50	122	65	149	....	....	95	203	125	257	150	302	165	329	96	2	Required	0.10	Red dye
Domestic	25	....do....	....do....	....	....	50	122	75	167	....	....	105	221	155	311	175	347	190	374	96	2	...do...	.10	
U. S. Government motor gasoline	16	.....	....do....	55	131	....	....	....	....	105	221	140	284	200	392	....	....	225	437	95	....	.....	.10	

Burning Oils

Name and grade	Color, darkest allowed	Flash point, Tag	Sulphur, maximum	Flock test	End point, maximum	Cloud test, maximum	Doctor test	Burning test	Photometric test	Reaction test	Flash point, Cleveland, minimum
	Saybolt No.	° *F.*	*Per cent*		° *F.*	° *F.*		*Hours*			° *F.*
Marine kerosene	16	115	0.125	Required	625	5	.....	16	.....	.....	.....
Marine kerosene (U. S. Navy)	16	115	.125	....do....	625	5	.....	16	May be required	.....	.....
Kerosene	16	100	.125	....do....	625	5	.....	16	.....	.....	.....
Long-time burning oil	21	115	.10	....do....	600	Zero	Required	168	.....	.....	.....
300° mineral seal	16	.....	.....	....do....	.....	32	.....	Special	.....	Required	250

Fuel Oils for Use in Oil Burners

Name and grade	Flash point, Pensky-Martens, minimum	Water, maximum	Sediment, maximum	Water and sediment, maximum	Furol viscosity at 77° F., maximum	Furol viscosity at 122° F., maximum	Sulphur, maximum
	° F.	*Per cent*	*Per cent*	*Per cent*	*Seconds*	*Seconds*	*Per cent*
Navy standard	150	.....	.....	1.0	100	.....	1.5
Bunker A	150	.....	.....	1.0	100	.....	.....
Bunker B	150	.....	.....	1.0	.....	100	.....
Bunker C	150	[a]1.75	[a]0.25	.....	.....	300	.....

[a] A deduction in quantity will be made for all water plus sediment in excess of 1.0 per cent.

Name and grade	Greases									Waxes		
	Viscosity at 100° F. of mineral oil, minimum	Calcium soap content, approximate	Moisture, maximum	Corrosion test	Ash	Soda soap content, minimum	Free alkali, NaOH	Color	Water, glycerin, and impurities, maximum of dry soap content	Name and grade	Color of melted wax	Melting point
	Saybolt seconds	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*		*Per cent*		*Saybolt No.*	° F.
Cup grease No. 0	100	13	3	Required	1.7	.....	.....	.....	.....	Paraffin:		
Cup grease No. 1	100	14	3	....do....	1.8	.....	.....	.....	.....	130 to 132....	25	130–132
Cup grease No. 2	100	16	3	....do....	2.0	.....	.....	.....	.....	124 to 127....	25	124–127
Cup grease No. 3	100	18	3	....do....	2.3	.....	.....	.....	.....	117 to 120....	25	117–120
Cup grease No. 5	100	24	3	....do....	3.5	.....	.....	.....	.....			
Recuperator grease	180	18	3	....do....	2.3	.....	.....	.....	.....			
Crank-pin grease	.....	.....	.....	.....	.....	40	0.5–2.5	Yellowish	33⅓			
Driving-journal compound	.....	.....	.....	.....	.....	45	.5–2.5	Greenish	33⅓			
Rod-cup grease	.....	.....	.....	.....	.....	40	.5–2.5	Yellowish	33⅓			

SPECIFICATIONS FOR LUBRICANTS AND LIQUID FUELS. REVISED MARCH 18, 1924—*Continued*

Lubricating Oils

Name and grade	Flash, minimum	Fire, minimum	Viscosity, Saybolt seconds				A. S. T. M. color, undiluted	A. S. T. M. color diluted 85 per cent	Pour, maximum	Acidity, maximum mg. KOH per gram	Corrosion test	Emulsion test	Demulsibility, minimum	Carbon residue, maximum	Precipitation, maximum	Compounding	Special tests required
			100° F.		210° F.												
			Minimum	Maximum	Minimum	Maximum											
	° F.	° F.	*Seconds*	*Seconds*	*Seconds*	*Seconds*			° F.					*Per cent*	*No.*	*Per cent*	
Class A, extra light	315	355	135	165	.....	.....	7	.....	35	.....	Required	.....	.....	.....	.....	.....	Reaction test
Class A, light	325	365	180	220	.....	.....	7	.....	35	.....	....do....	.....	.....	.....	.....	.....	
Class A, medium	335	380	270	330	.....	.....	7½	.....	40	.....	....do....	.....	.....	.....	.....	.....	
Class A, heavy	345	390	360	440	.....	.....	8	.....	45	.....	....do....	.....	.....	.....	.....	.....	
Class A, extra heavy	355	400	450	550	.....	.....	8	.....	50	.....	....do....	.....	.....	.....	.....	.....	
Class B, extra light	315	355	135	165	.....	.....	7	.....	35	.....	....do....	Required	300	.....	.....	.....	
Class B, light	325	365	180	220	.....	.....	7	.....	35	.....	....do....	....do....	300	.....	.....	.....	
Class B, medium	335	380	270	330	.....	.....	7½	.....	40	.....	....do....	....do....	300	.....	.....	.....	
Class B, heavy	345	390	360	440	.....	.....	8	.....	45	.....	....do....	....do....	300	.....	.....	.....	
Class B, extra heavy	355	400	450	550	.....	.....	8	.....	50	.....	....do....	....do....	300	.....	.....	.....	
Class C, extra light	315	355	135	165	.....	.....	7	.....	35	0 10	....do....	....do....	300	0.10	.....	.....	
Class C light	325	365	180	220	.....	.....	7	.....	35	.10	....do....	....do....	300	.20	.....	.....	
Class C, medium	335	380	270	330	.....	.....	7½	.....	40	.10	....do....	....do....	300	.45	.....	.....	
Class C, heavy	345	390	360	440	.....	.....	8	.....	45	.10	....do....	....do....	300	.55	.....	.....	
Class C, extra heavy	355	400	450	550	.....	.....	8	.....	50	.10	....do....	....do....	300	.70	.....	.....	
Class D, extra light	315	355	135	165	.....	.....	7	.....	35	.30	....do....	.....	.....	.10	.....	.....	
Class D, light	325	365	180	220	.....	.....	7	.....	35	.30	....do....	.....	.....	.20	.....	.....	
Class D, medium	335	380	270	330	.....	.....	7½	.....	40	.30	....do....	.....	.....	.45	.....	.....	
Class D, heavy	345	390	360	440	.....	.....	8	.....	45	.30	....do....	.....	.....	.55	.....	.....	
Class D, extra heavy	355	400	450	550	.....	.....	8	.....	50	.30	....do....	.....	.....	.70	.....	.....	
Class D, ultra heavy	360	410	.....	.....	55	65	....	5	50	.30	....do....	.....	.....	.80	.....	.....	
Class D, tractor	380	430	.....	.....	75	85	....	6	50	.30	....do....	.....	.....	1.50	.....	.....	
Class D, tractor, heavy	390	440	.....	.....	90	100	....	7	50	.30	....do....	.....	.....	1.75	.....	.....	
Class D, motor cycle	400	450	.....	.....	110	120	....	8	50	.30	....do....	.....	.....	2.00	.....	.....	
Aircraft machine gun	200	.....	80	115	.....	.....	.....	.....	—45	.10	....do....	.....	.....	.03	.....	.....	
Buffer	265	.....	65	75	.....	.....	.....	.....	Zero	.10	.....	.....	.....	.....	.....	.....	
Car and locomotive engine	300	.....	.....	.....	65	75	.....	.....	45	.....	.....	.....	.....	.....	0.5	.....	
Compounded steam cylinder	475	.....	.....	.....	120	150	.....	.....	60	.80	.....	.....	.....	.....	.5	5–7	

SPECIFICATIONS FOR LUBRICANTS AND LIQUID FUELS. REVISED MARCH 18, 1924—*Continued*

Lubricating Oils

Name and grade	Flash, minimum	Fire, minimum	Viscosity, Saybolt seconds				A. S. T. M. color, undiluted	A. S. T. M. color, diluted 85 per cent	Pour, maximum	Acidity, maximum mg. KOH per gram	Corrosion test	Emulsion test	Demulsibility, minimum	Carbon residue, maximum	Precipitation, maximum	Compounding	Special tests required
			100° F.		210° F.												
			Minimum	Maximum	Minimum	Maximum											
	° F.	° F.	*Seconds*	*Seconds*	*Seconds*	*Seconds*			° F.					*Per cent*	*No.*	*Per cent*	
Diesel engine	360				55	65			45	.30		Special		.80			Protection test
Gear, chain, and wire rope					900	1100											
Gun and ice machine No. 100	290		95	115					5	.10	Required	Required	300				
Gun and ice machine No. 125	290		120	135					5	.10	do	do	300				
Liberty Aero, grade 1	400				75	85			15	.10		Special		1.5	.5		
Liberty Aero, grade 2	400				90	100			30	.10		do		2.0	.5		
Liberty Aero, grade 3	450				90	100			45	.10		do		2.5	.5		
Liberty Aero, grade 4	450				115	125			45	.10		do				10-20	Wick-feed test
Marine engine No. 1				850	65	75			32	3.00	Required	do				10-20	Do.
Marine engine No. 2				850	65	75			45	3.00	do	do					
Mineral steam cylinder No. 1	475				135	165			60					4.5	.5		
Mineral steam cylinder No. 2	525				180	220			60					4.5	.5		
Recoil oil, light	225	250	40	45					−5	.10	Required						
Recoil oil, medium	315	355	140	160					−5	.10	do						
Recoil oil, heavy	345	390	385	430					−5	.10	do						
Electric switch	290		95	110					20	.10	do						Heat, breakdown and unsaturation tests
Transmission	460				135	165											

Class A covers grades of petroleum oil used for general lubrication where a highly refined oil is not required; only refined petroleum oils without admixture will be considered.

Class B covers grades of petroleum oil for lubrication of turbines, dynamos and high-speed steam engines using circulating and forced-feed systems.

Class C covers the grades used for lubricating *both* turbine and internal combustion engines.

Class D covers the grades of petroleum oils used by the government for lubrication of internal combustion engines, except aircraft, and Diesel engines.

CHARACTERISTICS OF THE FATTY ACIDS FROM SOME OILS

Oil.	Refr. Ind. at 60° C.	M.pt. °C.	Solidifn. Pt. °C.	Iodine Per cent.
Almond	1.4461	13–14	9–11.8	93.5–96.5
Castor	1.4546	13	3	86–88
Chinese wood	—	40–43.8	31.2	145-159.4
Cocoanut	1.4295	24–27	15–20	8.4–9
Codliver, Medicinal	—	—	17–18 (titer)	164–171
Corn	—	18–21.6	14–16	113–125
Cottonseed	1.446	34–40	32–35	105–112
Elaine				
Horse		37.5–39.5	33.6–37.7	84–87
Lard		35		
Linseed	1.4546	17–24	13–17	179 209.8
Menhaden	No figures av	ailable.		
Black Mustard	1.4665 at 20°	9–17	6–8	108–126.5
Neatsfoot	—	28.5–29.8	16–26.5 (titer)	62–77
Olive	1.4410	19–31	17–24.6	86–90
Palm	—	47.7–50	36–46 *44*	53.3
Peanut	1.4461	27–35	22–32.5	95–103
Poppyseed	1.4506	20–21	16.5	139
Rape	1.4491	16–22	16–18	99–105
Seal	—	14–33	13–17	186–202
Sesamé	1.4461	23–32	18–26	109–112
Sperm	—	13–21	16	83–99
Sunflower	1.4531	17–24	17–18	124
Tallow				
Whale	—	14–27	23–24	130–132

CHARACTERISTICS OF SOME OILS

Oil.	Sp.Gr. 15° C.	Refr. Ind. 15° C.	Valenta °C.	Elaidin.	Maumené °C.	Sap. No. mg.	Iodine %	Composition.	Common Adulterants.	Visc. U. Sec. 100° F.	Flash °F.[1]
Almond	0.914–.920 *.918*	*1.4738*	*110*	Solid	53	190–195.4	93–101 *97*	Olein, linoleim.	Peach and apricot kernel, cottonseed, peanut, lard, olive, sesamé and poppyseed.		
Castor	).959–.968	1.4795–.4803	Soluble	Solid	46–47	176–186	81–90	Ricinolein, stearin, dihydroxy stearin.	Blown oils, linseed, rape, cottonseed and rosin.	1485	505
Chinese wood or tung oil	0.940–.944	1.503 at 19°	40–47	Liquid and solid	—	190–197	156–176	Olein, elacomargarin.			
Cocoanut	0.926 0.874 at 99° C.	1.4573	—	—	—	225–268	8–10	Caproin, caprylin, caprin, olein, laurin, myristicin, palmitin, stearin.	Rarely adulterated.		
Codliver, medicinal	0.922–.941	1.478–1.481	—	Liquid and solid	100–116	183–188	135–198	Palmitin, stearin, jecolein, therapin	Salmon, seal, whale, shark liver; oils from other Gadidæ are not, commercially speaking adulterants.		
Corn or maize	0.921–.927 *.922*	1.4768	80	Pasty	56–88 *85*	189–193 *191*	111–123 *115*	Palmitin, arachidin, olein, linolein.	Rarely adulterated.	187	480
Cottonseed	0.921–.930 *.922*	1.4737–4757	90–110	Pasty	70–90 *76*	191–196	101–117 *108*	Stearin, palmitin, olein, linolin, arachidin.	Rarely adulterated.		
Elaine or Red	0.899–.908	1.4631 at 25° C.	—	Solid	—	200	90	Oleic, palmitic and stearic acids.	Cottonseed and mineral.		
Horse	0.916–.922	1.4652–.4704	54–80	—	46–55	195–197	75–86	Similar to lard but dries.	Rarely adulterated.		
Lard	0.914–.916	1.4694	54–98	Very solid	39–47 *43*	190–196	60–88	Olein, stearin, palmitin.	Cottonseed, tallow, corn and mineral.	214	565
Linseed	0.9315–.9371 *0.932–.926*	1.4835	57–79	Liquid and solid portion	103–126 *90*	187–195.2 *189–194*	167.6–205.4 *178–190*	Isolinolein, linolein, linolin, olein, stearin, palmitin.	Corn, cottonseed, fish and rosin.		
Maize	See Corn										

[1] With covered tester.

Menhaden	0.927–.936 *0.930*	1.4783	64	As linseed	123–128 *126*	189–193 *190*	139–193 *154*	Linolein, myristin, asellin, and acetin, clupanodonin.	Mineral and rosin.		
Bl'k Mustard	0.917–.919	1.4672	Insoluble	Pasty	42–43	173–176	98–110	Like rapeseed.	Sesamé.		
Neatsfoot	0.915-.916	1.4695–.4705	62–75	Solid at times	42 49.5	194–199	66–76	Olein, palmitin and stearin.	Other hoof oils, fish, poppy seed, rape, cottonseed and mineral oils.	224	440
Olive	0.915–.920 *.916*	1.4703 .4713	85–111	Very Solid	35–47 *41*	185–203 *190*	77–94 *82*	Olein, palmitin, arachidin and linolin.	Cottonseed, peanut, rape, sesamé, poppyseed and lard.		
Palm	0.920–.924 0.859 at 99° C.	1.451 at 60°	—	—	—	196 202	53–57	Palmitin, palmitic acid and stearin.	Water, sand and dirt.		
Peanut or Arachis	0.916–.925 *.917*	1.4731	87-112	Solid	46–75 *51*	185–197 *194*	83–105 *98*	Palmitin, linolin, olein, arachidin and lignocerin.	Cottonseed, rape, sesamé and poppyseed.		
Poppyseed	0.924–.927 *.925*	1.4773	—	Pasty	87	190–197 *193*	133–143 *138*	Linolin, linolein and isolinolein, olein, stearin, palmitin.	Sesamé.		
Rape or Colza	0.913–.917 *.916*	1.472–.4757	Insoluble	Pasty	49–64 *55*	168–178 *174*	94–106 *101*	Stearin, olein, erucin, rapin, and arachidin.	Cottonseed, poppyseed, hempseed, linseed, fish oil.	247	455
Seal	0.924–.933	1.477	—	Pasty	—	178–196 *188*	127–193 *147*	Palmitin, olein, hypogaein.	Mineral and rosin.	164	515
Sesamé	0.922–.924	1.4748–.4762	87–107	Pasty	63–72	187–194	103–115	Stearin, palmitin, olein and linolin	Cottonseed, peanut, rape and poppyseed		
Sperm	0.844–*.880* .884	1.4664–.4673	Insoluble	Solid at times	45–51	123–147	70–96	Contains no glycerin, palmitic acid.	Whale, mineral, rape, liver and arctic sperm.	115	455
Sunflower	0.924–.926	1.4762	—	Pasty	72–75	188–194	119–133	Linolin, olein.			
Tallow	0.916	1.4660 at 25° C.	71–75	Solid	35	197	56	Similar to lard.			
Turpentine	See page	617.									
Whale	.917–.927	1.4691 at 25°	—	Pasty	88	188–193	110–136	Palmitin.	Seal oil.	184	515

CHARACTERISTICS OF SOME WAXES

Wax.	Sp.Gr. 15° C.	Ref. Index. at 40°	M.pt.	Solid Pt.	Sapn. Value.	Acid Value.	Iodine Value.	Composition.	Common Adulterants.
Carnauba	0.99–.999	65–69°	83–91	80–87	79–88	0.3–7.0	5–13.2.	Ceryl and myricyl cerotate, carnaubate and a hydrocarbon.	Stearic acid, ceresin and paraffin.
Candelilla	0.969–.993	At 71.5° 1.455	65–68	63–68	46–65	10–21	14–36.8	Hydrocarbon, myricyl alcohol	Like carnauba wax.
Beeswax	0.959–.970	At 75° 1.439–1.445	62–70	60–63	87–107	16.8–21	7.9–11	Cerotic and melissic acids, myricin, ceryl and myricyl, alcohols, hydrocarbons.	Water, mineral matter, flour, starch, tallow, stearic acid, other waxes, rosin.
Chinese or Insect	0.970	—	80–81	80–83	80–93	51% fatty acids	1.4	Ceryl cerotate.	
Spermaceti	0.905–.960	—	41–46	41–47	120–134.6	49–53% fatty acids	3.8	Cetyl palmitate.	Stearic acid, beeswax, tallow, paraffin.
Woolfat or wax	0.941–.97	—	Acids 31–42	Acids 40	82–130	—	15–29	Ceryl and carnaubyl alcohols, cholesterol, lanoceric, lanopalmic, myristic, and carnaubic acids.	
These two below are really fats but are called waxes.									
Japan	0.975	—	50–51	48–50.8	217–237.5	—	4.2–15.1	Palmitin and palmitic acid.	Water, starch, other fats.
Myrtle	0.995	At 80° 1.436	40–48	39–45	205–217	—	1.9–3.9	Palmitin.	

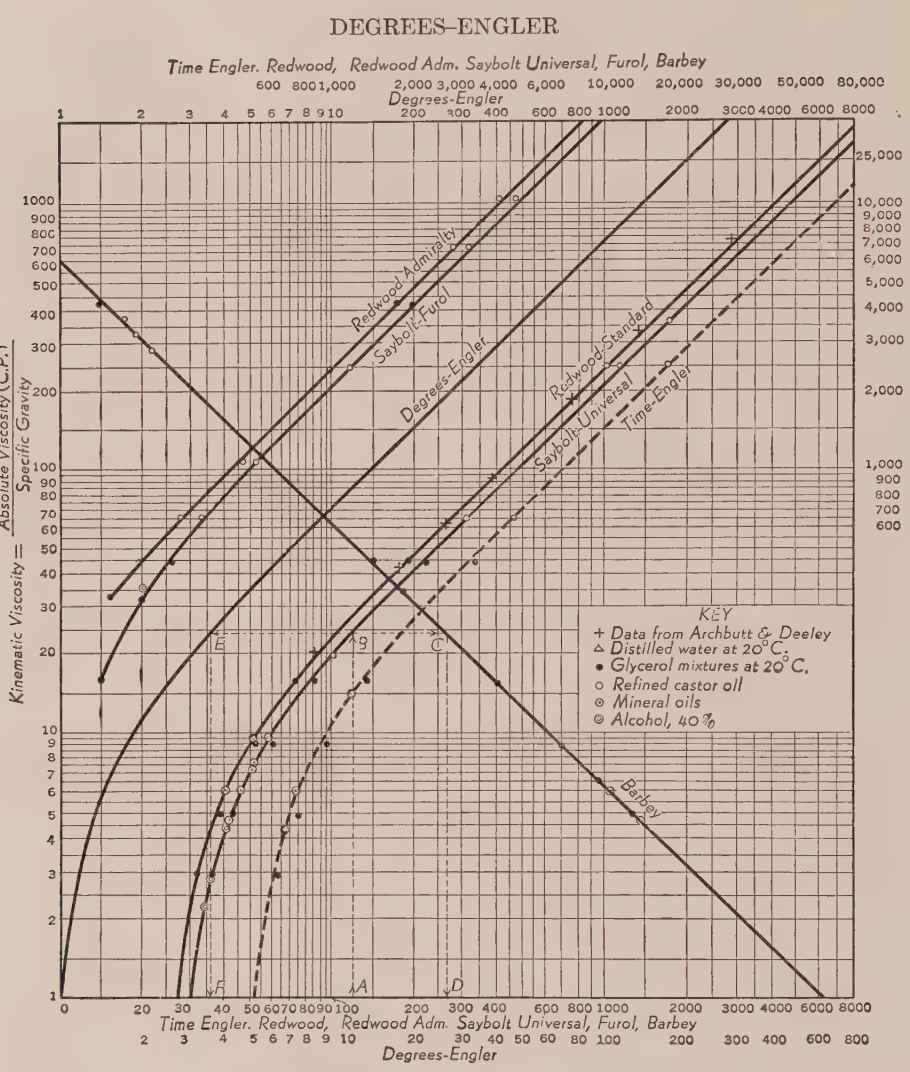

FIG. 258.—Viscosimeter Conversion Chart [150]

(Directions for Use of Chart)

OBJECT: To find the viscosity reading of a particular oil on any of the standard viscosimeters when its reading on one of the viscosimeters has been determined by experiment *at the same temperature.*

SCALES: There are two sets of scales which must not be confused with each other.

X: The scales at bottom and left hand side go together. They are the ones regularly used in practice applying to all ordinary oils.

Y: The scales at top and on right hand side go together. They are rarely used, applying only to very viscous products beyond range of other scales.

[150] Power (1922), 377.

NOTE.—There are two lines of scales at the bottom: (a) The lower scale applying only to degrees Engler. (b) The upper scale applying to all other readings, including Engler-time. In simply changing from one viscosimeter to another the scales at left and right are not used. The scales at top must never be used in connection with those at the bottom.

APPLICATION OF CHARTS: X: For ordinary cases.—GIVEN: Saybolt Universal Viscosity = 120″. DESIRED: Case (a) Barbey reading. Case (b) Engler-Degree reading. PROCEDURE: Find point on bottom scales for Saybolt Universal corresponding to 120″ (A). Follow up vertically to curve marked Saybolt Universal (the known instrument) (B). (a) To get Barbey reading: Follow horizontally to curve marked Barbey (C). Drop down to bottom scale for Barbey and read (C). Reading = 265 deg. (b) To get Engler-Degree reading: Follow horizontally to curve marked Degrees-Engler (E). Drop down to lower of the two bottom scales for Engler-Degrees and read (F). Reading = 3.62 deg., *i.e.*, 120″ Saybolt = Barbey 265 deg. = Engler 3.62.

Y: For very viscous fluids beyond range of other scales. GIVEN: Engler-Degrees = 1100 deg. DESIRED: Saybolt Furol reading. PROCEDURE: Find point on upper scales under Degrees-Engler corresponding to 1,100 deg. Follow vertically down to Degrees-Engler curve. Follow horizontally to curve marked Furol. Rise vertically to scales under Furol and read. Reading = 3800″, *i.e.*, 1,100 deg. Engler = 3,800″ Furol.

MULTIPLYING FACTORS TO REDUCE SAYBOLT TIMES TO ENGLER NUMBERS OR TO REDWOOD TIMES [1]

Saybolt Times Seconds.	Factor Saybolt Time to Engler Number.	Factor Saybolt Time to Redwood Time.	Saybolt Times Seconds.	Factor Saybolt Time to Engler Number.	Factor Saybolt Time to Redwood Time.
28	0.0357	0.95	75	0.0289	0.86
30	.0352	.95	80	.0286	.86
32	.0346	.94	85	.0284	.86
34	.0342	.94	90	.0282	.85
36	.0337	.94	95	.0280	.85
38	.0334	.93	100	.0279	.85
40	.0330	.93	110	.0276	.85
42	.0327	.92	120	.0274	.84
44	.0323	.92	130	.0272	.84
46	.0320	.91	140	.0271	.84
48	.0317	.91	160	.0269	.84
50	.0314	.90	180	.0268	.84
55	.0308	.90	200	.0267	.84
60	.0302	.89	....	.....	....
65	.0297	.88	1800	0.0267	0.84
70	0.0293	0.87			

[1] The Engler number is the quotient of Engler Time divided by the water value of the instrument at 20° C. in seconds.

Reagents

The reagents used in oil analysis are few and easily obtained. A list and their method of preparation is here given.[151]

Acetic Acid, Glacial. C.P., 99.5% pure. The determination of its strength should be made by titration and not by specific gravity, as the 98% and 80%

[151] Proc. Am. Soc. Test. Mat., 15, 1, 288, 1915.

acid have the same specific gravity, 1.067. The determination of the melting-point gives results equally good with those obtained by titration and requires less time.[152] It is made after the manner of the "titer test" (p. 1784), the tube being half filled, chilled to 10 to 11° C., and further chilled by placing the outside bottle in ice-water; the temperature of the super-cooled acid rises to its melting-point, where it remains stationary for some time. The melting-points of acids of various strengths are as follows:

100%, 16.75° C.; 99.5%, 15.65°; 99%, 14.8°.

For Hanus's solution it must not reduce potassium bichromate and sulfuric acid.

Acetic Anhydride.

Alcohol. Commercial "Cologne Spirits." For the preparation of alcohol free from aldehyde for alcoholic potash, cologne spirits are treated with silver oxide as follows: 1½ grams of silver nitrate are dissolved in 3 ml. of water, added to 1 liter of alcohol and thoroughly shaken; 3 grams of potassium hydrate are dissolved in 15 ml. warm alcohol and, after cooling, added to the alcoholic silver nitrate and thoroughly shaken again, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled, a few bits of pumice, prepared by igniting it and immediately quenching under water, being added to prevent bumping. Alcohol for use in the free acid determination is prepared by placing 10 to 15 grams of dry sodium carbonate in the reagent bottle, taking care to filter it before use.

Alcohol, Amyl.

Bromine. The commercial article; also a N/3 solution, made by dissolving 26.6 grams bromine in 1 liter carbon tetrachloride.

Calcium Chloride. The dry and also the crystallized salt.

Calcium Sulfate. Plaster of Paris.

Carbon Tetrachloride. Baker and Adamson's C.P. or Kahlbaum's "Tetrachlorkohlenstoff."

Chloroform. Squibb's, U. S. P.

Copper. Copper turnings or clippings, used for the generation of nitric oxide.

Copper Wire. Cut in pieces of 0.3 to 0.5 gram.

Ether. Squibb's, U. S. P.

Gasoline. Gasoline, 86° Baumé.

Hydrochloric Acid, C.P.—Specific gravity 1.2. For N/2 HCl dilute 39 ml. of the above acid to 1 liter and standardize.

Iodine Solution. Fifty grams of iodine to 1 liter of alcohol. For Hanus's solution dissolve by warming 13.2 grams iodine in 1 liter glacial acetic acid; cool and add 3 ml. of bromine.

Lead Acetate. One hundred grams of the salt to 1 liter.

Lacmoid. Three grams per liter of dilute alcohol.

Lacmoid Paper. Unsized paper dipped in above solution.

Litmus Paper.

Mercuric Chloride. Sixty grams of the salt to 1 liter of alcohol.

Nitric Acid. Specific gravity 1.34.

Phenolphthalein. One gram of the substance to 500 ml. of alcohol.

[152] McIlhiney, et al., J. Am. Chem. Soc., **29**, 1224, 1907.

Meta-Phosphoric Acid. A saturated solution of the commercial "stick phosphoric acid" in absolute alcohol.

Potassium Bichromate. Dissolve 3.8633 grams of the C.P. salt in 1 liter of water; 1 ml. is equivalent to 0.01 gram of iodine. The solution should be tested against iron wire containing a known percentage of iron.

Potassium Hydroxide. N/2: Dissolve 30 grams of "potash by alcohol" in 1 liter of alcohol. N/6: Dissolve 10 grams of "potash by alcohol" in 1 liter of water and dilute to proper strength. The solution should be protected by "stick potash" from the carbon dioxide in the air. *Ten per cent:* Dissolve 100 grams of "stick potash" in 1100 ml. of alcohol.

Potassium Iodate. A 2% solution.

Potassium Iodide. One hundred fifty grams of the commercial salt are dissolved in water and made up to 1 liter of water. This should be free from iodate, shown by yielding no coloration when acidified with strong HCl.

Silver Nitrate. Thirty grams to 1 liter+0.4 ml. HNO_3.

Sodium.

Sodium Chloride. Ordinary "coarse fine" salt for freezing mixtures.

Sodium Hydrate. 36° Baumé. Dissolve 300 grams of caustic soda in 1 liter of water.

Sodium Nitroprusside. The commercial salt.

Sodium Thiosulfate. N/10: Dissolve 26 grams of "sodium hyposulfite," in 1 liter of water.

Starch Solution. Rub up in a mortar 1 gram of potato starch, with 10 to 15 ml. of water, pour this into 200 ml. of water which is boiling actively, and continue the boiling for a few minutes.

Sugar. Ordinarily granulated sugar.

Sulfur. A 1.5% solution in carbon bisulfide.

Sulfuric Acid, C.P. This should be at least 99.5% pure, and its strength be determined by titration, as 100% and 94.3% acid have the same specific gravity.

Dilute. One part acid to ten parts water.

Nitrosulfuric Acid, for the Elaidin Test. A liter of sulfuric acid of 46° Baumé (1.47 specific gravity) is prepared by diluting 560 ml. commercial sulfuric acid to 1 liter; a few drops of nitric acid are added and nitric oxide (generated from copper and nitric acid) passed in until it is saturated. The acid is then cooled in ice-water and the gas passed in until it is saturated at 0° C. This is called Roth's liquid.

The author wishes to acknowledge his indebtedness to Mr. Thomas T. Gray for his careful review of this chapter. Mr. Gray's broad experience in petroleum products as Chief Chemist of Tidewater Oil Company, makes his criticism and suggestions of special value.

[153] Richmond, J. Soc. Chem. Ind., 9, 479, 1890.

JUNKER'S CALORIMETER FOR LIQUID FUELS

Directions for Working

1. Filling the lamp: Loosen the wing screw *b*, remove the arm with the gauge and pour about 150–200 cm.^{3} of fuel into the recipient. Then put the gauge arm on again and close the opening by again tightening the screw.

2. Setting up: Place the balance by the side of the calorimeter so that the burner of the lamp hangs exactly in the center of the combustion chamber of the calorimeter, after which the lamp with its appendage *g* is hung from one arm of the scales and counterbalanced by putting weights on the other scale. By using a mirror the right position to be obtained can be easily controlled. The lamp can be turned around the appendage *e*, when the nut *f* is loosened.

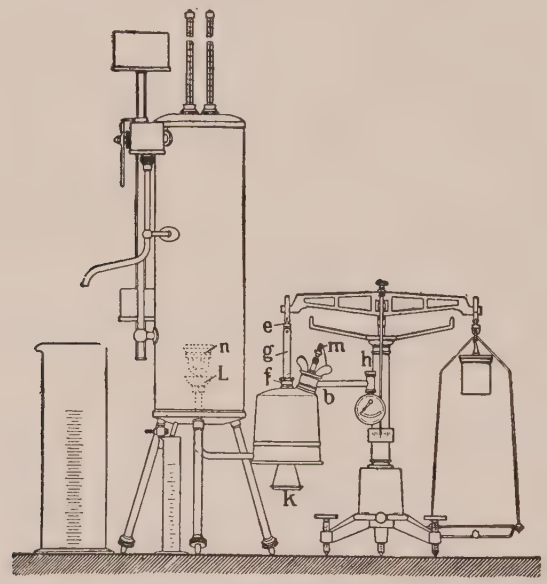

Fig. 258a.

3. Starting: Remove the lamp again from the balance, fill the cup *L* beneath the burner heat with spirit and light it. Then take the hood *m* and screw the air hose of the air-pump to the valve. When the spirit of small cup is nearly burnt out, press air into the recipient by vigorously pushing the air piston; the air acting upon the fuel, it will rise into the burner and gasify on its hot surface. The gas streaming out of the nozzle ignites itself on the spirit flame and feeds the gasification, even when the spirit is completely burnt out.

If no gas streams out, the nozzle *n* is obstructed; it must be cleaned by means of the special pin included with the apparatus. An ordinary pin must not be used as in doing so damage would be done to the nozzle.

4. Regulation: Press as much air into the apparatus that a uniform and free burning flame is obtained. (The development of heat should be about 1000 calories per hour, thus about 100 grams of petroleum, benzine or lubricating oil, or 130 grams of spirit must be burnt per hour.)

If the flame is too large, the screw *h* should be slightly slackened so as to let some air escape. When the flame is well regulated, the small wing screw of the valve is tightened again, the pump is removed and the small hood *m* is screwed on the thread.

5. Measuring: Now introduce the burner into the combustion chamber beneath the calorimeter and hang the lamp on one arm of the balance as indicated but *not before having filled the calorimeter with water so that it flows out at the outlet.*

After having introduced the lamp, the thermometer at the water outlet begins to rise. By means of the regulating cock of the calorimeter the water supply must be regulated thus, that the difference between the inflowing and outflowing water is about 10–20°. After having reached the state of permanency, *i.e.*, when the thermometer does not rise any more, put a small weight on the scale *k* so that the arm of the balance goes down. The balance will only reach its state of equilibrium when a certain amount of fuel has been burnt.

The moment when the pointer of the balance reaches the point of zero, the hose must be turned over the gauge. At the same time the cup *k* is charged with 10–20 grams. After this, begin reading the two thermometers, doing this preferably at regular intervals. The trapping of the water and the reading is interrupted the moment where the lamp again starts rising and the hand goes again through *o*. At this point 10–20 grams of fuel have been burnt.

The higher heating value is calculated according to

$$H = \frac{W}{G} T,$$

where H is the heating value in calories per gram,
W the quantity of the water trapped in kilos or liters,
G the quantity of fuel consumed, in grams,
T the difference of temperature between inflowing and outflowing water.

Heating value of a kilogram $= 1000H$.

In order to ascertain the lower heating value, the condensed water flowing off is caught in a small gauge, the number of milliliters of collected condensed water obtained from 10 grams of burnt fuel is multiplied by 60 and the number thus obtained is deducted from the upper heating value of a kilogram of fluidity, found in the calorimeter.

6. Stopping the calorimeter: Slacken the screw *h* of the lamp whereby the pressure of air will cease at once and the flame will be extinguished.

Annotations: The burner head with the small nozzle is designed for fuels rich in carbon (as petroleum, benzine, etc.), that with the large nozzle for fuels containing water (spirit). The more carbon, the smaller the bore. Spirit requires the smallest pressure of air, under 200 millimeters; mineral and lubricating oil the highest. Vegetable and animal oils must be used for combustion only if they are completely volatilized at a boiling point of 250°

at the highest. Thus, several oils cannot be used, for instance, neat's foot oil, rape oil, olive oil.

Mineral lubricating oils may be used, if they evaporate completely at 250°.

If the preliminary warming is not sufficient, or the pressure of the air is too high, the burning is subject to sudden shocks; by slackening the screw *h* and warming up again, this inconvenience will be done away with.

When lubricating oil has been burnt, the lamp must be well cleaned with petroleum followed by benzine. Then the lamp should be soaked with a quantity of the liquid fuel which is to be tested. Only when this has been done, the liquid fuel for a new measuring may be poured into it.

There is no danger whatever of explosion, even with benzine, as the flame will never get back into the recipient, as the pipe and the small nozzle are always filled with fluid. Naturally benzine should not be poured into the recipient in the proximity of the burning lamp.

THE DETERMINATION OF TETRAETHYL-LEAD IN GASOLINE [154]

Two hundred (200) ml. of the gasoline sample, measured in a volumetric flask, are chilled in ice water for at least ten minutes and then poured into a 500-ml. separatory funnel, supported in a ring stand.[155]

Place a chemically clean 600-ml. beaker under the separatory funnel. This is done at the start to avoid loss in case a drop of the concentrated Pb solution, subsequently formed, should seep past the stopcock. Add very slowly (dropwise at first) and with gentle agitation, 20 ml. of a solution of 1 part by volume of C.P. liquid bromine (Br) and 2 parts of carbon tetrachloride (CCl_4). Let stand with occasional shaking for fifteen minutes. Add ten ml. of concentrated C.P. nitric acid and *agitate carefully*, avoiding loss due to gas pressure. Allow the acid to settle and draw it off into the 600-ml. beaker. Wash down the sides of the funnel with about 20 ml. of distilled water and draw off the water into the beaker. The wash water at this point is to facilitate drawing off the most concentrated Pb solution without loss through dripping from the stem of the funnel and without drawing off any of the gasoline layer. Repeat the acid and water washing as outlined above, agitating somewhat more vigorously. Make three final water washes of about 50 ml. each and shake thoroughly with these portions.

The beaker should now contain all the Pb in solution. It should contain very little gasoline because by the above procedure it is not necessary to draw off the aqueous layers very close to the gasoline line. Boil the solution in a

[154] By R. H. Pierson, Chief Chemist of the Gilmore Oil Co., Ltd.

[155] NOTE.—Reasonable care should be exercised to avoid contamination of the Pb solutions from the use of wire on stopcocks and stoppers of separatory funnels, and from metallic ring supports. Considerable amounts of fumes of Br, HBr, CCl_4 and gasoline are evolved in the shaking procedure, and fine wire is usually used to avoid loss of stoppers through the force of the gas pressure generated. If wire is used, it is well to tie cloth over it to prevent any stray drops of acid from carrying metal into solution. Such metal can be removed by subsequent procedure, but it is preferable to avoid loss of time so occasioned.

good hood until the volume of liquid is reduced to 30 or 40 ml. Dilute to 100 ml. with distilled water and filter. Make the clear filtrate just ammoniacal, using litmus paper as indicator. Bring just acid to litmus with weak acetic acid and add an excess of only five or six drops of glacial acid. Heat nearly to boiling and add 10 ml. of a 10% solution of $K_2Cr_2O_7$. Boil three or four minutes to coagulate the $PbCrO_4$, filter hot through a tared asbestos Gooch crucible, wash well with water, and dry in an oven at 100° C.

Finally, ignite as follows: Place the Gooch crucible inside a wide form porcelain crucible and heat the outer crucible with a small bunsen flame. The flame should be about one inch in height and its top should just touch the bottom of the crucible. The $PbCrO_4$ will darken slightly, which is normal. Excessive heating should be avoided; it is only necessary to bring about complete dehydration. Cool and weigh the Gooch crucible. Calculate to Pb or $Pb(C_2H_5)_4$ by the following factors:

$$PbCrO_4 \times 0.6411 = Pb,$$
$$PbCrO_4 \times 1.0006 = Pb(C_2H_5)_4.$$

The following factors apply on the basis of the 200-ml. sample as outlined in the procedure.

g. $PbCrO_4$ weighed $\times 3.2055$ = g. Pb per liter of gasoline.
g. $PbCrO_4$ weighed $\times 5.003$ = g. $Pb(C_2H_5)_4$ per liter of gasoline.

Taking into account also the specific gravity of $Pb(C_2H_5)_4$, g. $PbCrO_4 \times 11.415$ = ml. $Pb(C_2H_5)_4$ per U. S. gallon of gasoline.

It is not difficult by the above method to obtain results on duplicate tests which check within 0.05 ml. $Pb(C_2H_5)_4$ per gallon when working on gasolines containing about 2 ml. per gallon. In general, check determinations should not show more than 2% variation.

Determination of Nitrobenzine in Oils Used for Oiling Floors

Procedure.—Shake 20 ml. of oil with 1 ml. of concentrated HOAc until homogeneous, add about 0.2 g. of Zn powder, heat until the odor of $PhNO_2$ is gone, cool, decant into a separating funnel, wash the excess Zn 3 times with 1 ml. of diluted HOAc and after filtering these washings add them to the funnel, shake, let stand, separate the red-brown lower layer and divide into 2 parts. (1) To 1 part add 2–3 vols. of Et_2O and a " pinch " of PbO_2. The liquid immediately turns violet and on agitation the Et_2O absorbs this color. (2) To the second part also add Et_2O as before and then a few drops of aqueous $K_2Cr_2O_7$. The aqueous layer becomes green, then yellow-red, and in the Et_2O the same violet color appears as with PbO_2. By means of standard color tubes which are prepared under the same conditions with known amounts of $PhNO_2$ in a hydrocarbon oil the amount of $PhNO_2$ in the oil under investigation can be estimated. About 0.05 per cent $PhNO_2$ is the minimum which can be detected. The intensity and tone of the colors are influenced by the conditions of the reactions, so that both the amounts of liquids and the conditions must be carefully controlled. The use of a colorimeter serves to increase the precision of the test.[156]

[156] Pietro Biginelli, Atti congresso naz. chim. ind. **1924**, 274–6. C. C. Davis, C. A. **19**, 1391, May, 1925.

PETROLEUM AND ITS PRODUCTS. TESTING AND INTERPRETATION OF RESULTS[1]

The modern refining methods with the growing demand of greater efficiency, better products and the reclaiming of former waste products places petroleum chemistry in a very important place in the chemical industry. The testing of crude oils and their products determines the methods used in refining and gives an accurate evaluation of the oils to be refined.

Petroleums may be classed as paraffin, asphaltic and mixed base crude. The paraffin base petroleum is made up of the straight chain hydrocarbons having a formula C_nH_{2n+2}. They are saturated hydrocarbons and are not acted upon by sulfuric acid. The asphaltic base contains the naphthenes (C_nH_2n) or cyclic compounds and aromatic hydrocarbons. The mixed crudes are a combination of paraffin and asphaltic compounds.

Petroleums frequently have other compounds than the hydrocarbons mentioned, such as the compounds containing oxygen, nitrogen, and sulfur. These may be of industrial significance but are generally considered as the undesirable qualities which should be removed. Foreign matter such as water, sand, clay and asphalt may be found as suspensions and emulsions. The information as to their presence may avoid much trouble in the distillation as they often form the emulsifying agents for permanent emulsions or decrease the temperatures in which " cracking " begins.

The increased demand for gasoline has increased the " cracking " of the higher molecules and has made the tests for unsaturates, carbon in colloidal form, fixed gases and gases containing gasoline, of great importance in most commercial plants.

The reclaiming of the waste matters and the making of by-products by the treating of the fractions containing the sulfur and nitrogen compound makes a careful and accurate testing of these compounds of greatest importance.

The examination and evaluation of the petroleums and their products should be done in an accurate and systematic manner, so that the combined results will give a workable knowledge. The complexity of the petroleums or their fractions makes most tests have little value or they may be very misleading unless accompanied by other data. The conclusions arrived at should be verified by other tests and a complete report made as to the results.

The following tests mentioned will be found in detail in other parts of this text. Each test should have a definite point to determine and all data recorded in a logical manner.

[1] Contribution by Robert C. Beckstrom.

TESTS MADE ON CRUDE PETROLEUM AND ITS PRODUCTS, INCLUDING THE INTERPRETATION OF RESULTS

Crude Oils

The Physical Tests.—The color of petroleum gives little information unless other than green or black. Other colors may indicate contamination with clays, sands or water.

Odor.—The odor of petroleum may indicate in a general way the fields from which the oil came. A gasoline indicates a pure paraffin base crude with high gasoline content. The aromatic and pyridine odors are common to some of the crude oils from California, Texas, Rumania, Russia, and is found in shale oils. The odor of pyridine is more pronounced if the sample is agitated with potassium hydroxide solution. A slight terpene odor may be detected in some of the Gulf Coast oils.

The specific gravity or Baumé gravity [2] of a crude indicates the approximate amount of light oils. This test should be followed by the distillation of the crude oil for an accurate determination.

The test for sediment and water (page 1761) determines the need of dehydration, the types of stills used for refining or whether it will be accepted for pipe line transportation. In the heavier crudes, water may be in such small droplets that considerable care must be taken to complete the separation.

The fractional distillation of petroleum gives a fair determination of the amounts of gasoline, kerosene, fuel oil, and lubricating oil. It is found that any one method of distillation for the different kinds of petroleums is unsatisfactory when fractions are identified by their boiling points alone. These results should be supplemented with other tests. The asphaltic and mixed base petroleums begin to crack at lower temperatures than the paraffin base petroleums and the products of distillation will be found to be much different. A crude oil with emulsions or finely dispersed particles of water in it must first be dehydrated before a distillation can successfully be made.

STANDARD METHOD OF TEST FOR DISTILLATION OF CRUDE PETROLEUM [3]

A. S. T. M. Designation: D 285–36 [4]

Scope.—This method is intended for determining the percentages and distillation range of the naphtha in any crude oil of the class commercially known as refinable crudes. This method does not attempt to specify what quality of product shall be defined as naphtha nor can it be expected to duplicate the

[2] The specific gravity $= \frac{141.5}{131.5+\text{Bé}}$.

[3] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[4] This method is issued under the fixed designation D 285; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1928; Adopted in Amended Form, 1933; Revised, 1936. This method has been approved as American Standard by the American Standards Association.

results of commercial refining operations. It defines apparatus and procedure, leaving selection of numerical limits and interpretation of results to be agreed upon by the interested parties.

Apparatus.—***Flask.***—The distillation flask shall be of the type illustrated in Fig. 259, the dimensions and allowable tolerances being as follows:

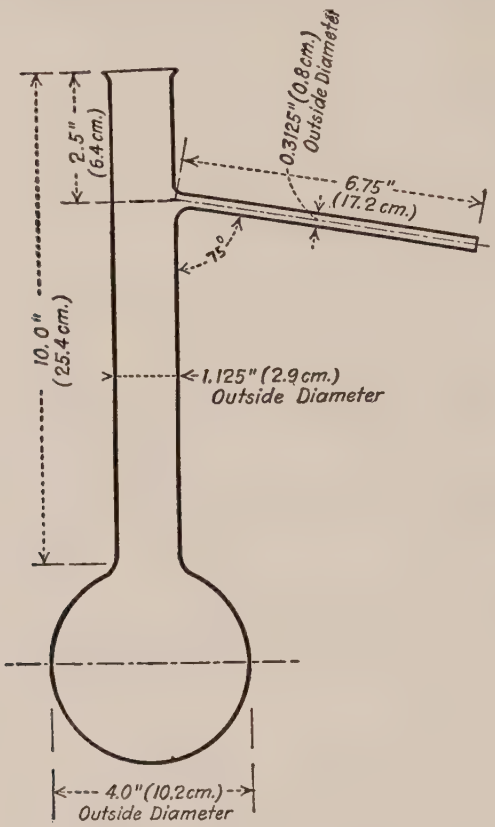

FIG. 259.—Distillation Flask.

	Centimeters	Inches	Tolerances	
			Centimeters	Inches
Diameter of bulb, outside	10.2	4.0	±0.2	±0.08
Diameter of neck, outside	2.9	1.125	±0.1	±0.04
Length of neck	25.4	10.0	±0.4	±0.16
Distance, top of neck to center of vapor tube	6.4	2.5	±0.3	±0.12
Length of vapor tube	17.2	6.75	±0.5	±0.20
Diameter of vapor tube, outside	0.8	0.3125	±0.1	±0.04

The vapor tube shall be set at an angle of 75°±5° with the neck of the flask.

Fractionating Column.—The fractionating column (see *a*, Fig. 260) shall be made of a length of No. 18 iron jack chain, enough to pack under its own weight into a column 2.54 cm. (1 in.) in diameter and 16.51 cm. (6½ in.) in length. It may conveniently be " strung " on a loop of wire so that it hangs in loops about 2 ft. in length, which makes the chain more convenient to handle than when it is not looped together. The device used for supporting the column (see *b*, Fig. 260) shall be made of a suitable length of wire, preferably, though not necessarily of nickel-chromium, about No. 18 gage. One end shall be wound in a spiral a little less than 1 in. in diameter, and the remaining wire shall be bent at right angles to the plane of the spiral and cut off at a length of about 9½ in. A small loop shall be bent into the end away from the spiral and put through a hole drilled in a strip of spring steel (see *c*, Fig. 260) or other suitable material about 0.015 in. in thickness, ⅜ in. in width, and 3 in. in length, bent around a cylinder 1 in. in diameter. When allowed to expand this spring strip should hold firmly on the inside of the neck of the flask and provide a secure support for the column of chain.

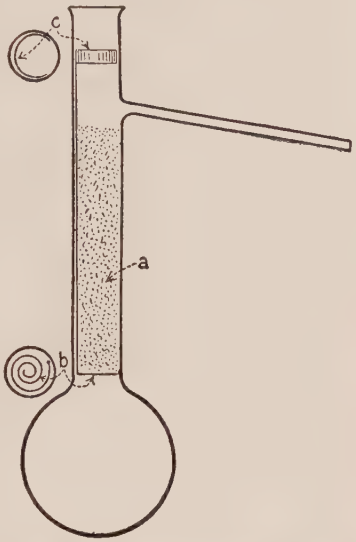

Fig. 260.—Fractionating Column and Supporting Device in Hempel Flask.

Thermometer.—The A. S. T. M. Low-Distillation Thermometer, conforming to the requirements specified in Section 6 (*a*) of the Standard Method of Test for Distillation of Gasoline, Naphtha, Kerosene, and Similar Petroleum Products (A. S. T. M. Designation: D 86) of the American Society for Testing Materials [5] shall be used.

Condenser.—The condenser shall consist of a $\frac{9}{16}$-in. (14.29-mm.) OD No. 20 Stubbs Gage seamless brass tube, 22 in. (55.88 cm.) in length. It shall be set at an angle of 75° from the perpendicular and surrounded with a cooling bath 15 in. (38.1 cm.) in length, approximately 4 in. (10.16 cm.) in width, by 6 in. (15.24 cm.) in height. The lower end of the condenser tube shall be cut off at an acute angle, and curved downward for a length of 3 in. (7.62 cm.) and slightly backward to insure contact with the wall of the graduate 1 to 1¼ in. (2.54 to 3.18 cm.) below the top of the graduate when it is in position to receive the distillate.

Shield and Support.[6]—The shield shall be of any convenient type having a minimum horizontal dimension of 6 in. The flask shall rest on a board of ¼-in.

[5] 1936 Book of A. S. T. M. Standards, Part II. See p. 1705.

[6] An illustration of the condenser and of a suitable shield and support are shown in Fig. 2 of the Standard Method of Test for Distillation of Gasoline, Naphtha, Kerosene, and Similar Petroleum Products (A. S. T. M. Designation: D 86) of the American Society for Testing Materials, see 1936 Book of A. S. T. M. Standards, Part II.

(0.64-cm.) transite or hard asbestos, in the center of which is cut a hole 3½ in. (8.9 cm.) in diameter. The board shall not be less than 6 in. (15.24 cm.) in width and shall be supported by an ordinary ring stand and ring.

Gas Burner or Electric Heater: (*a*) *Gas Burner.*—The burner shall be so constructed that sufficient heat can be obtained to distill the product at the uniform rate specified below. The flame should never be so large that it spreads over a circle of a diameter greater than 5 in. (12.7 cm.) on the under surface of the asbestos board. A sensitive regulating valve is a necessary adjunct, as it gives complete control of heating.

(*b*) *Electric Heater.*—The electric heater, which may be used in place of the gas flame, shall be capable of maintaining the distillation at the rate specified in Procedure (*i*). The electric heater shall be fitted with an asbestos board top ⅛ to ¼ in. (3.18 to 6.35 mm.) in thickness having a hole 3½ in. (8.9 cm.) in diameter in the center. When an electric heater is employed the portion of the shield above the asbestos board shall be the same as with the gas burner, but the part below the board may be omitted.

Measuring Graduates and Pipettes.—Filling charges and distillation fractions shall be measured with suitable accurate graduated cylinders or other volumetric glassware. A 300-ml. pipette with unconstricted outlet, similar to Fig. 261, is a convenient device for measuring charges, but an accurate graduate may be used if desired. The regular 100-ml. graduate used in gasoline distillations as specified in Section 7 of the Standard Method of Test for Distillation of Gasoline, Naphtha, Kerosene, and Similar Petroleum Products (A. S. T. M. Designation: D 86) of the American Society for Testing Materials[7] is reasonably satisfactory for measuring distillation fractions, but a graduate of similar dimensions that can be tightly stoppered is preferable. One can be made by cutting down a standard graduate to remove the lip and then fire polishing.

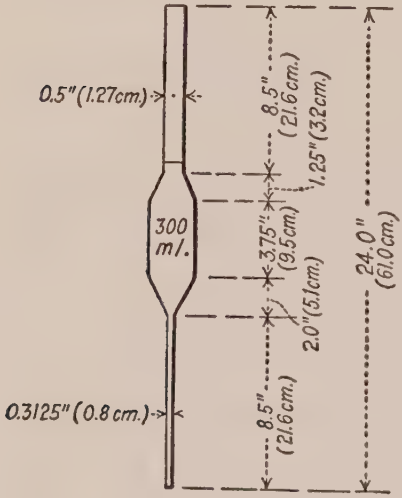

FIG. 261.—Measuring Pipette.

Procedure. — (*a*) The condenser bath shall be filled with cracked ice and enough water added to cover the condenser tube. The temperature shall be maintained between 32° and 34° F. (0 and 1.1° C.). Any other convenient cooling medium may be used provided these temperature conditions are maintained.

(*b*) The condenser tube shall be swabbed or cleaned inside to remove any liquid remaining from a previous test.

(*c*) The specific gravity of the oil to be tested shall first be determined in accordance with the Standard Method of Test for Gravity of Petroleum and

[7] 1936 Book of A. S. T. M. Standards, Part II.

Petroleum Products by Means of the Hydrometer (A. S. T. M. Designation: D 287) of the American Society for Testing Materials.[7]

(*d*) A quantity of the oil [8] equivalent to 300 ml. at 60° F. (15.5° C.) shall be measured or weighed into the distillation flask by any suitable means. None of the liquid shall be permitted to flow into the vapor tube.

(*e*) The supporting device for the fractionating column, Fig. 260, shall be put in place and the proper quantity of iron chain dropped in carefully so that it fills the space uniformly and without channels. Tapping the flask while the iron chain is being added is helpful, but the column shall not be compressed after all the chain is in place.

(*f*) The thermometer, provided with a cork, shall be fitted tightly into the flask, so that it will be in the middle of the neck and so that the lower end of the capillary tube is about $\frac{1}{16}$ in. below the level of the inside of the bottom of the vapor tube at its junction with the neck of the flask.

(*g*) The charged flask shall be placed in position on the hard asbestos board, used with the gas burner or the electric heater and connected to the condenser with a carefully fitted cork through which the vapor tube passes. The position of the flask shall be adjusted so that the vapor tube extends into the condenser tube not less than 1 in. (2.54 cm.) nor more than 2 in. (5.08 cm.).

(*h*) A clean, dry, graduated cylinder shall be placed at the outlet of the condenser tube in such a position that the condenser tube shall extend at least 1 in. into the graduate. The graduate shall be immersed up to the level of about 1 in. below the tip of the condenser tube in a transparent container of water maintained at a temperature of from 32 to 40° F. (0 to 4.4° C.). During the distillation, the top of the graduate shall be covered closely with a piece of blotting paper or its equivalent, cut to fit the condenser tube tightly.

(*i*) When everything is in readiness, heat shall be applied. The fractionating column causes some little delay between the time when the liquid starts to boil and the time the vapor enters the condenser. It is, therefore, permissible to apply heat vigorously until the liquid begins to boil, then to slow down the application of heat so that the distillate begins to come over at a moderate rate. For the first 5 to 10 ml. distilled the rate shall be from 2 to 3 ml. per minute; thereafter, the rate of distillation shall be increased to from 4 to 5 ml. per minute.

(*j*) ***Distillation.***—When the thermometer reads . . .[9] the graduate shall be withdrawn from beneath the condenser and the distillation discontinued. The graduate shall be tightly stoppered and allowed to stand until all sediment and moisture have settled out and until its contents have reached a temperature between 55 and 65° F. The total volume in the graduate shall then be read and recorded as *D*. The volume of water, if any, shall be read and recorded as *W*.

The percentage of naphtha in the crude oil shall be calculated from the following formula:

$$\text{Percentage of naphtha} = \frac{D - W}{300 - W} \times 100$$

[8] In case the water content of the crude oil causes bumping, or in any case if the crude oil contains more than 2 per cent of water, the sample shall be dehydrated by some suitable method, without loss of naphtha, before making the determination.

[9] The temperature at which the distillation shall be stopped can best be decided by mutual agreement between the parties concerned in the evaluation of a given crude petroleum.

The whole procedure shall be repeated enough times to yield a total volume of distillate of not less than 100 ml.

Naphtha Distillation.—The distillates shall be poured together (taking care to avoid losses by evaporation and rejecting the layers of water, if present) and shall be mixed thoroughly by shaking. A distillation test of the combined distillates shall be made in accordance with the Standard Method of Test for Distillation of Gasoline, Naphtha, Kerosene, and Similar Petroleum Products (A. S. T. M. Designation: D 86) of the American Society for Testing Materials,[10] except that the initial boiling point shall be recorded and the volume of distillate collected in the cylinder shall be observed and recorded to the nearest 0.5 ml. when the mercury of the thermometer reaches 212° F. (100° C.), 221° F. (105° C.), 284° F. (140° C.), 392° F. (200° C.) and the end point.

Accuracy.—Results of duplicate tests in the crude-oil distillation should not differ from each other by more than 0.5 per cent.

Correction for Barometric Pressure.—The actual barometric pressure shall be ascertained and recorded, but no correction shall be made except in case of dispute, when the temperature points shall be corrected to 760 mm. (29.92 in.) by the use of the Sydney Young Equation, as follows:

For Centigrade Readings:

$$C_c = 0.00012(760 - P)(273 + t_c)$$

For Fahrenheit Readings:

$$C = 0.00012(760 - P)(460 + t_f),$$

in which C_c and C_f are, respectively, corrections to be added to the observed temperature t_c or t_f; and P is the barometric pressure in millimeters of mercury.

Sulfur may be detected by the odor of hydrogen sulfide or the mercaptans when a crude is heated. The sulfur tests as outlined on pages 1713 and 1756 give the quantitative measurements. The fact that sulfur is found in a petroleum does not follow that it will be equally divided in the distilled fractions. The author has found sulfur in varying amounts in the 10% fractions of the same crude oil with a slight variation in the method of refining. The importance of sulfur tests is not in the crude oil but in the products of distillation.

Gasoline, Naphtha

The specific gravity, Baumé or A. P. I., is taken with a hydrometer (page 1704). This information without other data, such as the distillation curve or the knowledge of its being a straight run, natural gasoline, or blended product, is of little value in the determination of the quality of the gasoline.

The yellow color in a gasoline (test, page 1742) indicates improper treatment with acid or sodium plumbite solution. A dark color may be caused by contamination with heavier hydrocarbons in pipe line or tank cars, and should not be confused with colors caused by other methods.

The sweet ethereal odors of gasoline are characteristic of the gasolines from low sulfur paraffin base crude oil. Sour or " cracked " odor is characteristic

[10] 1936 Book of A. S. T. M. Standards, Part II. See p. 1705.

of a gasoline incompletely refined and it is probably made from a high temperature cracking process.

The distillation test (page 1807) should be made with great care as a change in the rate of distillation, rapid or slow heating during the process gives inaccurate results. The distillation curve indicates a straight run, natural gasoline or blended product. The distillation range of a motor gasoline should conform to the following: [11]

Overpoint not more than 131° F.
20% recovered in receiver not more than 221° F.
50% recovered in receiver not more than 284° F.
90% recovered in receiver not more than 392° F.
End point not higher than 437° F.
At least 95% of distillate recovered.

The sodium plumbite test (page 1742) when positive indicates sulfur compounds that will cause the gasoline to turn yellow in storage. The gasoline giving a negative test may upon standing in the sunlight later give a positive test. This shows that the treatment of the gasoline has been incomplete and further treatment is needed. The sodium plumbate treatment may not decrease the sulfur content and may increase it. It does, however, cause the sulfur compounds to become more stable so as not to cause the gasoline to become yellow.

The testing for unsaturates (tests, pages 1766–1767) or the test by the United States Bureau of Mines [12] may be used. The Maumené (page 1766) test is to be used only as a check as it is unreliable for highly unsaturated mixture.

U. S. Bureau of Mines Test.—Five ml. of the gasoline are run into a clean, dry Babcock cream bottle and when cooled in ice water 200% by volume of sulfuric acid (1.84 sp.gr.) is added. A rubber stopper is then placed in the bottle and shaken with a rotary motion for several minutes. The gasoline and sulfuric acid then are separated by adding sulfuric acid until the surface is about level with the upper graduation mark on the neck of the bottle. The bottle is allowed to stand twelve hours or it can be placed in a centrifuge and whirled at the rate of 500 to 1000 R.P.M. for three minutes. A reading of the volume of gasoline remaining is then made and the loss to sulfuric acid is calculated.

The unsaturation gives information as to the amount of acid needed for the acid treatment. A highly unsaturated finished product may cause the deposition of carbon and gummy matter in the cylinder of the motor. This point is not accepted by all authorities.

Corrosion and gumming test (page 1742) indicates elementary sulfur compounds in the gasoline. The gummy material may be acid residues, polymerization of highly unsaturated compounds or asphaltic bodies.

[11] Bulletin 323A, United States Bureau of Mines.
[12] Tech. paper 181.

STANDARD METHOD OF TEST FOR GUM CONTENT OF GASOLINE [14]

A. S. T. M. Designation: D 381–36 [15]

Scope.—This test is a means of determining the amount of gum existent at the time of test in gasoline and other motor fuels boiling within the gasoline range. The results are indicative of the amount of gum deposition which may take place in service if the gasoline is used immediately but give no indication of the gum stability of the gasoline upon storage. Results obtained by this test are comparative only, inasmuch as the amount of gum residue obtainable from a given sample varies with the conditions of evaporation. In cases where the sample contains other dissolved non-volatile material, such as lubricating oil, such material may be obtained as residue along with possible gum; such samples obviously require special treatment, depending on the nature of the non-volatile material.

Apparatus.—The apparatus shall consist of the following:

(*a*) ***Beakers.***—Berzelius-type beakers of heat-resistant glass, without lip, of 100-ml. nominal capacity.

(*b*) ***Bath.***—The bath shall consist of a closed vessel provided with a reflux condenser, a well into which the beaker fits, a coil for preheating the air as prescribed in the Procedure, and a conical adapter to deliver the air into the center of the beaker. A suitable form of apparatus is shown in Fig. 262. A multiple bath having similar provisions is also satisfactory. The bath shall be filled to within 1 in. of the top with a stable liquid having a boiling point within a temperature range from 320° to 330° F. (160° to 165.8° C.), ethylene glycol containing approximately 3% water being suitable for the purpose. The bath shall be insulated with asbestos. An electric hot plate capable of keeping the liquid boiling actively is the preferred heating means. In the absence of a satisfactory hot plate the bath may be heated by a gas burner, in which case the apparatus shall be placed in a hood with a good draft.

(*c*) ***Air Supply.***—Low-pressure air, passing through a cotton or glass-wool filter and delivered to the preheater inlet of the bath. A flow meter or other air-measuring device shall be provided as shown in Fig. 262. The flow meter shall be calibrated when attached to the bath with the bath liquid at room temperature.

Procedure.—(*a*) The test beaker together with a similar tare beaker shall be washed free from gum with a mixture of equal volumes of benzol and alcohol, immersed for at least 12 hr. in chromic-acid cleaning solution and washed thoroughly first with tap water and then with distilled water. Subsequent to removal from the cleaning mixture the beakers shall be handled only by means of a clean, dry, metallic holder. After washing, both beakers shall be dried thoroughly by heating to about 302° F. (150° C.), and then allowed to cool

[14] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[15] This method is issued under the fixed designation D 381; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1934; Adopted in Amended Form, 1936.

simultaneously for the same period of time, but not less than 1 hr. in a desiccator. If the air in the balance to be used is dried with a desiccant then this same desiccant shall be used in the desiccator; otherwise no drying agent shall be used in the desiccator. The test beaker shall then be weighed, using its tare (Note) on the opposite balance pan. After weighing, the tare beaker shall be replaced in the desiccator and the test beaker shall be placed in the well of the bath as shown in Fig. 262. The air flow shall be adjusted to a rate at the point of measurement of 1 liter per second $\pm 15\%$. The bath shall then be heated

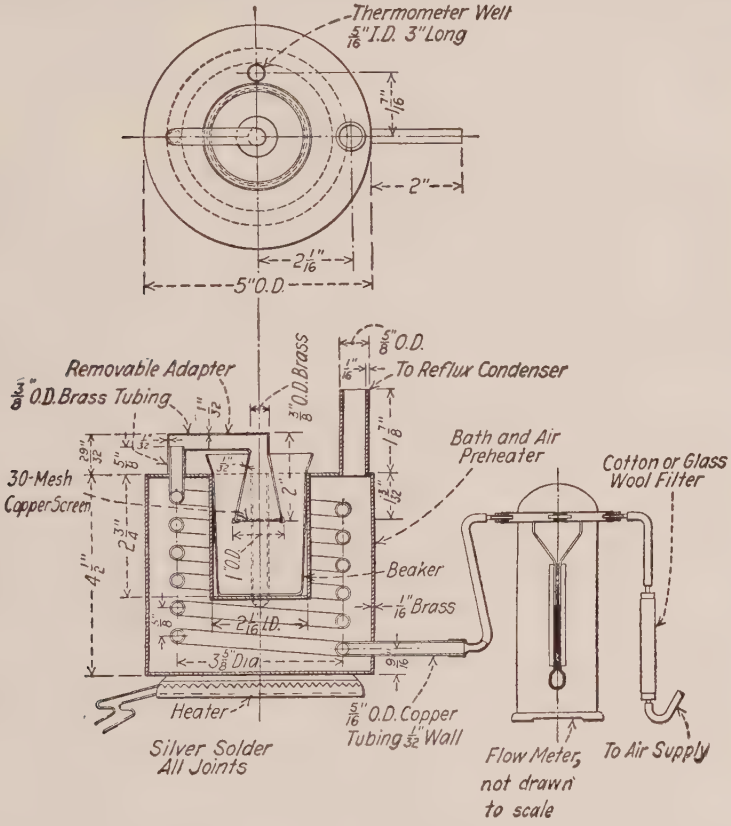

Fig. 262.—Apparatus for Determining Gum Content of Gasoline.

so that the temperature of the effluent air, measured by a thermometer placed on the bottom of the beaker at the center, shall be from 305° to 320° F. (151.7° to 160° C.). This is governed largely by the rate of boiling of the bath liquid and the rate of air flow.

Note.—For routine tests it is permissible to use the same beaker as a tare for more than one test beaker but not for more than six test beakers, provided all are heated at the same time.

(*b*) The conical adapter shall be removed and 50 ml. of the gasoline poured into the beaker after which the adapter shall be replaced on the air outlet so that it is vertically above the center of the surface of gasoline. After the gasoline has evaporated, which should require from 8 to 14 minutes, the beaker shall be left in place for an additional 15 minutes, the air supply being maintained. During this 15-minute period the tare beaker shall also be heated to about 302° F. (150° C.). Both test and tare beakers shall then be allowed to cool simultaneously and for the same period of time, but not less than 1 hr., in a desiccator under the same conditions as prescribed in Paragraph (*a*), and the test beaker weighed as before the test. The increase in weight of the test beaker represents the amount of gum in the sample.

Results.—Duplicate determinations shall be made and results shall be expressed in milligrams of gum per 100 ml. of gasoline.

Accuracy.—Results obtained by different operators in different laboratories should not differ by more than the following values:

For gum contents of	0 to 20 mg. per 100 ml	4 mg.
For gum contents of	20 to 100 mg. per 100 ml	10 mg.
For gum contents above	100 mg. per 100 ml	20 mg.

Duplicate results obtained by a single operator should not differ by more than one-half the above values.

Vapor Pressure determinations give direct information as to the probable behavior of motor fuels as regards easy starting and " flexibility." It indicates, if the pressure is high, the blending of natural gasoline with a straight run product. It is important in the shipping of gasoline in tank cars [13] and must conform with interstate shipping laws.

Kerosene, Mineral Seal and Gas Oil

Specific Gracity.—The specific gravity, Baumé or A.P.I., is determined by the same methods as described under gasoline. The test indicates approximately where the fraction has been cut during the distillation of the crude oil. This must be confirmed by other data such as the distillation curve, flash and fire points.

The dark colors show incomplete acid treatment, percolation or contact filtration. A " cracked " odor is the result of high temperatures or pressures during distillation, but may be removed with acid treatment.

The viscosity tests (page 1718) must conform to the specification for fuel oils under working temperatures. The oils should be free from water, dirt, and tarry matter which may clog the burners.

The cloud test (page 1727) indicates too deep a cut into the lubricating fraction and the settling out of crystals of paraffin. A fuel oil showing a cloud test will solidify when in storage during cold weather.

The distillation test determines the cause for the decrease of the illuminating power of the oil after burning for a time. In absorbing oils for " casing head gas " the distillation curve may determine its usefulness as an absorbing oil. A fraction having an over point much higher than the end point of the gasoline is desirable.

[13] Bureau of Explosive Circular MCL, No. 147.

The flash and fire tests (page 1702) must meet the specifications of illuminating and burning oils. A low flash and a high fire indicates a mixture of light fractions with the heavy fractions, making a poor fuel for the burners. The flame will not be uniform and the higher fractions will not burn but change into a vapor in the fire box, causing explosive mixtures. The test determines the fire hazard and is the real measure of inflammability. Most states have a law stating the minimum flash and fire points of illuminating oils.

The sulfur determinations (pages 1712, 1756) are of great importance in illuminating oil as they produce disagreeable odors during the burning period, and cause a charring of the wicks. The amount should not exceed .1%. Fuel oils when atomized with steam form sulfuric acids which cause rapid deterioration of boilers and pipe stills.

Lubricants

The determination of specific gravity of a lubricating oil (page 1704) may give information as to the nature of the petroleum from which it is made. A high Baumé gravity and a very high viscosity may indicate a lubricant that has been mixed with soaps, resins, or oils other than mineral oils.

The color of lubricating oils indicates the source of the oil. A turbid oil indicates finely divided droplets of water, or if cooled an amorphous wax. A dark-colored oil should be examined under a microscope for suspended carbon. When the oil is diluted with naphtha, the foreign matter held in suspension settles out.

The viscosity test (page 1718) has been regarded as a most important test of lubricants. The working temperature of the bearing should determine the temperature at which the test is made. Most lubricants have the same viscosity at 300° F. A lubricating oil functions only when a continuous film of oil separates the wearing surfaces and the oil is efficient when its viscosity allows this film to be continuous without a break in the film. The true test for a lubricating oil under working conditions is the machine for which it is to be used.

The cloud test (page 1727) indicates the temperature at which the paraffin wax separates from the oil solution. It shows whether the process for the separation of wax has been well done and gives the quality of the wax which is separated out. If the wax is amorphous in character, the oil must either be redistilled or centrifuged to remove this wax.

The pour test (page 1730) indicates the temperature under which an oil will flow. Knowing the working temperatures that the oil will be used will determine whether it will be an efficient lubricant.

The flash and fire test (page 1732) should be above the working temperatures of the bearing. High flash and burning points indicate good quality and careful refining. Too low flash and fire test results in a large loss from evaporation under working conditions.

The carbon residue test (page 1737) gives information in the laboratory approximating working conditions with the lubricants, producing more or less carbon deposits. A large per cent of residue indicates oils thickened by other matter or badly refined.

The demulsibility test (page 1740) determines the value of a lubricant which is to be used in forced feed lubrication and motor cylinders. A high degree of

emulsification indicates an oil containing an emulsifying agent such as sulfur compounds, salts of napthenic and other organic acids.

The fatty acid test (page 1736) when more than 15%, unless found in a cutting oil, will cause the formation of metallic soaps which clog the lubricating channels.

The test for rosin (page 1781) when found positive indicates an adulterated lubricating oil and is always objectionable.

Free sulfuric acid indicates poor refining methods and should not exceed .01% in transformer oils.

TENTATIVE METHOD OF TEST FOR NEUTRALIZATION NUMBER OF PETROLEUM PRODUCTS AND LUBRICANTS [16]

A. S. T. M. Designation: D 188–27 T [17]

Scope.—The methods described herein are designed to indicate in petroleum products and lubricants and compounded products the presence of organic constituents having acid characteristics and the contamination by alkalies and mineral acids.

Definitions.—(*a*) The Neutralization Number is the weight in milligrams of potassium hydroxide required to neutralize one gram of oil.

Note.—The Neutralization Number expresses the total amount of the mineral acid, and of the organic constituents having acid characteristics.

(*b*) The Alkali Neutralization Number is defined as the weight of acid required to neutralize one gram of oil, expressed in equivalent milligrams of potassium hydroxide.

(*c*) The Mineral Acid Neutralization Number is the number of milligrams of potassium hydroxide required to neutralize the mineral acid content in one gram of oil.

Solutions Required.—(*a*) ***Aqueous Potassium Hydroxide*** (1 ml. = 5 mg. KOH).—Dissolve 5.1 g. of potassium hydroxide, c.p., in one liter of freshly boiled and cooled distilled water. Add a very small amount of barium hydroxide, sufficient to precipitate any potassium carbonate present. Standardize this solution against Bureau of Standards certified benzoic acid, using phenolphthalein as an indicator according to the relation:

$$\frac{5 \text{ mg. KOH}}{x \text{ mg. benzoic acid}} = \frac{56.104 \text{ g. KOH}}{122.048 \text{ g. benzoic acid}}$$

1 ml. of KOH = 10.88 mg. benzoic acid.

This weight of benzoic acid is required for standardization.

[16] Criticisms of this Tentative Method are solicited and should be directed to Mr. R. P. Anderson, Secretary of Committee D-2 on Petroleum Products and Lubricants, 250 Park Ave., New York City. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[17] This is a Tentative Standard, published for the purpose of eliciting criticism and suggestions, and as such is subject to annual revision. Issued, 1925; Revised, 1926, 1927. This method has been approved as American Tentative Standard by the American Standards Association.

Make necessary adjustments so that the value of potassium hydroxide equals 5 mg. KOH per 1 ml.

NOTE.—Fit the solution bottle with a guard tube of soda lime to prevent access of carbon dioxide. The solution should be standardized at necessary intervals.

The weight of benzoic acid should be dissolved in 50 ml. of 95% alcohol and titrated cold. For blank, use same amount of alcohol and correct the titration.

(*b*) ***Sulfuric Acid Solution*** (1 ml. = 5 mg. KOH).—Match a sulfuric acid solution so that 1 ml. of the acid will be required to neutralize 1 ml. of the KOH using phenolphthalein as an indicator, titrating in boiling solution.

(*c*) ***Neutralized 95% Alcohol.***—Add a few drops of phenolphthalein and neutralize carefully the alcohol to a very faint pink end point with some of the above prepared alkali solution.

(*d*) ***Phenolphthalein Indicator.***—Dissolve 10 g. of the indicator in 1 liter of 95% alcohol, preferably ethyl. Use 1 ml. of this strength for titration.

(*e*) ***Methyl Orange Indicator.***—Dissolve 1 g. of the indicator in 1 liter of distilled water. Use 0.1 ml. of this strength fortitration.

Methods.—***Method A.—Neutralization Number of Petroleum Products.***—Weight of Oil: Approximately 20 g. weighed to 0.1 g.

Volume of Solvent: 100 ml. of a mixture of 1 : 1 neutralized alcohol and distilled water.

Procedure: Agitate oil and solvent thoroughly and heat to boiling. Add 1 ml. of phenolphthalein indicator and titrate rapidly, with vigorous agitation, to a sharp pink end point. The titration must be completed in a hot solution, reheating same if found necessary.

The color change is noted in the alcohol water layer.

Calculation:

$$\frac{(\text{Milliliters of KOH}) \times 5}{\text{Weight of oil taken}} = \text{mg. KOH per 1 g. of oil.}$$

Method B.—Neutralization Number of Compounded Petroleum Products.—Weight of Oil: Approximately 10 g. weighed to 0.1 g. Volume of Solvent: 50 ml. of neutralized alcohol.

Procedure: Agitate oil and solvent thoroughly and heat to boiling. Add 1 ml. of phenolphthalein indicator and titrate rapidly, with vigorous agitation, to a sharp pink end point. The titration must be completed in a hot solution, reheating same if found necessary.

The color change is noted in the alcohol layer.

Method C.[18]***—Alkali or Mineral Acid Neutralization Number in Non-Compounded and Compounded Petroleum Products.*** Weight of Oil: 25 to 50 g. weighed to 0.1 g. Volume of Solvent: Boiling distilled water, 200 ml.

Procedure.—Introduce into a 250-ml. separatory funnel 25 to 50 g. of oil weighed to 0.1 g., and add 100 ml. of boiling distilled water. Shake vigorously, and after oil and water have separated, drain the water layer into a 500-ml. casserole. Wash the oil in the separatory funnel twice by vigorously shaking with 50-ml. portions of boiling distilled water and after separation, drain into the casserole. To the accumulated 200 ml. of water add 1 drop of 1% phenol-

[18] When the oil is acid, the acidity shall not be reported as sulfuric or hydrochloric unless the presence of these acids shall have been confirmed by tests.

phthalein solution. Boil. If solution turns pink, add 1 ml. of the indicator and titrate with the sulfuric acid solution until the extraction is colorless.

If the addition of 1 drop of phenolphthalein causes no change in color, add 0.1 ml. of methyl orange. If color changes to red or pink, titrate with the KOH solution until the red color is just discharged.

An equal volume of distilled water shall be titrated with the standard solution used, and the amount of alkali or acid required shall be subtracted from the titration for blank correction.

Calculation: If the acid solution was required to discharge the phenolphthalein end point, the alkali neutralization number equals:

$$\frac{(\text{Milliliters of acid}) \times 5}{\text{Weight of oil}}$$

If the alkali solution was required to discharge the methyl orange end point, the mineral acid neutralization number equals:

$$\frac{(\text{Milliliters of alkali}) \times 5}{\text{Weight of oil}}$$

The evaporation test (page 1726) is used in testing lubricating oils used in high vacuum machines, transformer oils and air compressor oils. A high evaporation loss indicates light oils used in blending. It may be used in testing the dilution of " crank case " oil.

STANDARD METHOD OF TEST FOR DILUTION OF CRANKCASE OILS [19]

A. S. T. M. Designation: D 322–35 [20]

Scope.—This method is intended for the determination of the amount of dilution in crankcase oils of engines when gasoline has been used as the fuel.

Apparatus.—(*a*) ***General.***—The apparatus shall consist of a glass flask, heated by a gas-burner flame, and provided with a reflux water condenser discharging into a trap for collecting the distillate. The trap serves to collect and measure the diluent, returning condensed water to the still.

(*b*) ***Trap.***—The trap shall be made of well-annealed glass constructed in accordance with Fig. 263. It shall be graduated from 0 to 12.5 ml. in 0.1-ml.

[19] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants.

This method comprises a revision of the Standard Method of Test for Dilution of Crankcase Oils (A. S. T. M. Designation: D 322–33), 1933 Book of A. S. T. M. Standards, Part II, p. 768, which method it supersedes.

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[20] This method is issued under the fixed designation D 322; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1930; Adopted, 1933; Revised, 1935. This method has been approved as American Standard by the American Standards Association.

divisions. The error of any indicated capacity shall not be greater than 0.05 ml.

(*c*) ***Flask.***—The glass flask shall be of the short-neck, round-bottom type, with a nominal capacity of 1 liter.

(*d*) ***Condenser.***—The condenser shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length with an inner tube 9.5 to 12.7 mm. (⅜ to ½ in.) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 60°.

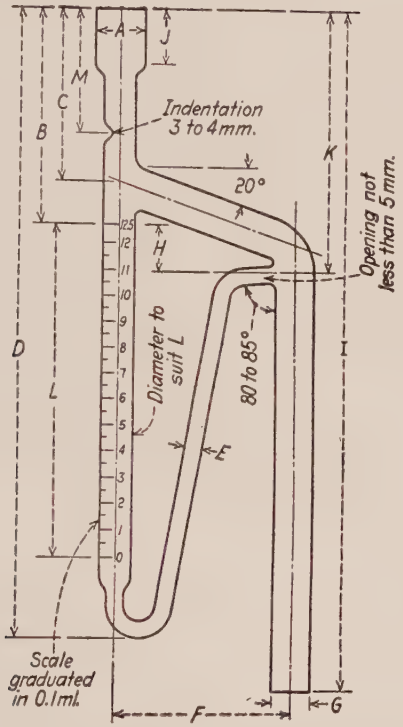

FIG. 263.—A. S. T. M. Dilution Trap for Testing Crankcase Oils.

A	18 to 20 mm., inside diameter	*H*	15 to 20 mm.
B	85 to 90 mm.	*I*	270 to 290 mm.
C	70 to 75 mm.	*J*	25 to 30 mm.
D	240 to 260 mm.	*K*	100 to 110 mm.
E	4 to 5 mm., inside diameter	*L*	125 to 138 mm.
F	65 to 75 mm.	*M*	40 to 50 mm.
G	11 to 15 mm., inside diameter		

(*e*) ***Burner.***—The gas burner shall preferably be of the Meker type, 1 in. in diameter, and the orifice used should be such that a narrow flame coming to a point about 4 in. above the top of the burner can be obtained.

Procedure.—The sample shall be mixed thoroughly, and 25 ml. shall be

measured into a 25-ml. graduate and transferred to the flask. By washing out the graduate with hot water only a negligible amount of oil will be left in the graduate. Approximately 500 ml. of water shall then be added to the flask and the apparatus shall be assembled, after filling the trap with water. The tip of the condenser shall be placed directly over the indentation in the trap.

Heat shall be applied with the full flame as indicated above. The rate (Note 1) shall be such that refluxing starts within from 7 to 10 minutes after the heat is applied, the water being at room temperature initially. The success of the method depends upon heating at such a rate that boiling is continuous and vigorous enough to prevent the oil from forming, even momentarily, a continuous film on top of the water. (Note 2.)

Note 1.—As a check on the rate of distillation, a determination may be made on a fresh oil containing 15% of added diluent. The oil used should have a flash point of 400° F. or over and the diluent used should have an initial boiling point of 300° to 320° F. and an end point of 400° to 420° F. At least 13.5% of the diluent should be obtained by this method on boiling for 60 minutes.

Note 2.—Bumping with a tendency to froth over is often experienced with dirty oils and may be prevented in several ways, namely, by the addition of bits of broken glass, by the addition of steel wool, or by the addition of about 5 ml. of concentrated HCl.

Readings of the amount of diluent shall be made at the following times, taken from the time that refluxing starts: 5, 15 and 30 minutes, and each 15 minutes following, until the test is complete. Completion of the test shall be determined on the basis of either or both of the following criteria:

No. 1.—Test is complete when the volume of diluent increases by not more than 0.1 ml. in any 15-minute period during the course of the test.

No. 2.—Test is complete when the volume of diluent obtained in a given time indicates completion, as follows:

Time from Start of Refluxing	Test Is Complete if Apparent Volume of Diluent Collected Is Equal to or Less Than
5 minutes	0.1 ml.[a]
30 "	2.0 ml.
60 "	4.0 ml.
90 "	7.0 ml.

[a] Report as "no dilution."

Generally criterion No. 1 defines the completion of the test, but when the test continues to a point at which any of the conditions described under criterion No. 2 are encountered, the latter shall define the completion of the test.

When the test is complete by either of the criteria above the heat shall be turned off. After standing at least 15 minutes, to allow the distillate to settle clear and to cool to approximately room temperature, the volume of diluent shall be read. The percentage dilution is obtained by multiplying this final volume by 4.

Accuracy.—Determinations by independent operators should agree within 20% for dilutions under 5% and within 10% for dilutions over 5%. Duplicate determinations by the same operator should, in general, show a closer agreement than the above.

STANDARD METHODS OF ANALYSIS OF GREASE [21]

A. S. T. M. Designation: D 128–27 [22]

Scope.—These methods of analysis permit determinations sufficiently accurate for referee purposes of all the constituents of greases likely to be covered by specifications. These constituents are fillers and ash, soap bases, soap, fat, water, excess alkali or acid, petroleum products and unsaponifiable matter. No quantitative determination of glycerin is described, but a procedure is outlined for its qualitative detection.

Sample.—The size of sample for the soap determination (Methods (1) and (2) for Determination of Fillers, Soap, Fat, Petroleum Oil and Unsaponifiable Matter) shall be from about 8 to 30 g., depending on the consistency of the grease, which is chiefly determined by the percentage of soap present. Ten to twenty grams is usually a convenient amount for No. 3 Cup Grease, while thin transmission and other greases require a larger sample. The original sample should be stirred or mixed until uniform.

Samples need not be weighed more closely than 0.1 g.

Solvents.—The **petroleum ether** shall have an end point not higher than 200° F., and 125 ml. of it shall not consume more than 0.2 ml. of 0.5 N potassium hydroxide when a blank test is made as follows:

One hundred and twenty-five milliliters of petroleum ether shall be boiled with 10 ml. of 0.5 N alcoholic potassium hydroxide and 50 ml. of neutral 50% alcohol for 1½ hours on a hot plate, using a glass tube of about 7 mm. internal diameter and 75 cm. long as a reflux condenser. After cooling, the solutions shall be titrated with 0.5 N hydrochloric acid and phenolphthalein. Not less than 9.8 ml. of 0.5 N acid shall be required for neutralization. The amount of alkali consumed in this test shall be deducted as a blank correction in the fat determination on solution (*E*).[23]

The ***alcohol*** shall be prepared from commercial 95% grain or denatured grain alcohol by distilling from sodium hydroxide, diluting to 50% (or 70%) by volume with distilled water and neutralizing exactly with sodium or potassium hydroxide and phenolphthalein.

The ***phenolphthalein*** solution shall be prepared by dissolving 1.0 g. of phenolphthalein in 50 ml. of strong redistilled alcohol, adding 50 ml. of water, and neutralizing with sodium or potassium hydroxide.

Concentrated c.p. hydrochloric acid shall be used when "concentrated hydrochloric acid" is specified. Hydrochloric acid, 10%, shall contain 10% by weight of absolute HCl, with a permissible variation of ±0.5%.

[21] Under the standardization procedure of the Society, these methods are under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[22] These methods are issued under the fixed designation D 128; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1922; Adopted in Amended Form, 1927. These methods have been approved as American Standard by the American Standards Association.

[23] Solutions designated by capital letters in parentheses refer to the solutions given in Fig. 264.

Procedure.—(*A*) ***Determination of Ash.***—The percentage of ash shall not be included in the total of the analysis.

NOTE.—The determination of the total ash should not in general be regarded as of any great importance. It is, however, sometimes required. This determination is often unsatisfactory on account of interaction between sodium carbonate derived from the soap, and inorganic fillers. There is always likelihood of reaction with the porcelain crucible itself on account of the long continued heating necessary to burn out all carbon. Moreover, if much sodium or potassium carbonate is present, the ash is fusible and often encloses carbon, making complete removal of the latter very difficult. Results will always be low in the presence of easily reducible oxides of volatile metals. There is also uncertainty as to when calcium carbonate has been completely ignited to calcium oxide. Ash determinations made on the same sample in different laboratories are likely to vary widely. For these reasons, it is usually preferable to make separate determinations of the percentage of fillers and of soap, from which data a calculation is easily made giving all the information to be gained from a direct determination of total ash.

(1) *Rapid Routine Method of Ash Determination.*—From 2 to 5 g. of grease shall be placed in a weighed porcelain crucible, and the sample weighed to the nearest 0.1 g. If lead or zinc soap is known to be absent, a platinum crucible is more convenient. The combustible matter shall be burned off slowly and the residue finally ignited until the ash is free of carbonaceous matter. The crucible and contents shall then be cooled in a desiccator and weighed, reporting the result as percentage of ash.

(2) *Alternative Method of Ash Determination.*—The sample shall be burned as in method (1) until the ash is nearly free from carbon. The crucible and contents shall then be cooled, the soluble portions dissolved in a little water, and a slight excess of dilute sulfuric acid added, running the acid in carefully from a pipette inserted under a small watch glass covering the crucible. The crucible and contents shall then be warmed on the steam bath until effervescence has ceased. The watch glass shall then be rinsed with water into the crucible. The solution when tested with methyl orange for free acidity shall show free acid present. The contents of the crucible shall be evaporated to dryness, and the whole ignited at a low red heat, adding a few small pieces of dry ammonium carbonate to drive off the excess of sulfur trioxide. After cooling and weighing, the result shall be reported as " percentage of ash as sulfates."

The alternative method gives more concordant results than the first method, but requires more time and manipulation.

(*B*) ***Qualitative Examination of Ash.***—*Detection of Bases.*—An easily fusible ash, dissolving completely in water to give a strongly alkaline solution, indicates a grease containing sodium, potassium, or both. A white infusible ash, practically insoluble in water, but imparting to it an alkaline reaction, may indicate calcium, with or without magnesium or aluminium. Zinc is shown by the yellow color of the ash while hot, and lead may be indicated by the presence of metallic globules, or by the yellow color of the ash when cold.

The ash shall be dissolved in dilute nitric or hydrochloric acid, and the presence of the several bases confirmed by suitable chemical tests, any standard scheme of qualitative analysis being followed.

(*C*) ***Quantitative Examination of Ash.***—For the quantitative examination of ash any standard analytical procedure shall be used, the choice of methods

being based on the information gained from the qualitative tests. If only one base is present, a quantitative determination is in general unnecessary.

(*D*) ***Determination of Fillers, Soap, Fat, Petroleum Oil and Unsaponifiable Matter.***—Cup, fiber and sponge greases, with or without graphite, and all comparatively light colored greases, including axle greases, shall be examined by method (1). Dark greases containing residuum, asphaltic oils and asphalt, tars, etc., shall be examined by method (2), as these ingredients usually cause stubborn emulsions if a shaking-out process is applied at the start.

(1) *Determination of Filler, Soap, Fat, Etc.*—If no fillers are present, the grease sample shall be introduced directly from a weighing bottle into a separator, the weight of the sample being obtained by difference. The sample shall then be shaken with 75 ml. of petroleum ether and 50 ml. of 10% hydrochloric acid until the grease is completely decomposed, after which the procedure given under Determination of Soap shall be followed. If fillers are present, the sample (See Sample) shall be weighed in a small beaker, 50 ml. of 10% hydrochloric acid added and the beaker, warmed on the steam bath, stirring until all soap lumps have disappeared and the upper layer is clear. If undissolved mineral matter or other filler is present, both layers shall be filtered through a Gooch crucible provided with a suitable mat, the beaker and crucible washed with water and petroleum ether, and the crucible finally washed with strong alcohol, the alcohol washings being collected separately and discarded. The crucible and contents shall then be dried at 120° C. and weighed, and the result reported as " percentage of insoluble matter " (graphite, mica, talc, asbestos, gypsum, wood pulp, etc.).

Determination of Gypsum.—If gypsum is present as a filler, the results obtained in the determination described under Fillers, etc. will be too low because of the solubility of calcium sulfate in hydrochloric acid. A sample of about 5 g. of grease shall be weighed in a small beaker, and decomposed with 50 ml. of petroleum ether and 25 ml. of concentrated hydrochloric acid, warming on the steam bath until all gypsum is dissolved. The contents of the beaker shall be cooled and poured into a separatory funnel, the beaker rinsed with water and a little petroleum ether and the solutions in the funnel allowed to separate clearly. The lower layer shall then be drawn into a beaker, and the petroleum ether in the separator washed with two portions of 20 ml. each of 10% hydrochloric acid, and the washes added to the strong acid solution in the beaker. The hydrochloric acid solution in the beaker shall then be evaporated on the steam bath almost to dryness, diluted of 150 ml. with water, heated to boiling and treated with 10 ml. of 10% barium chloride solution. The barium sulfate shall then be filtered off and ignited in the usual way, and from the weight of the barium sulfate, the percentage of calcium sulfate shall be calculated, reporting it as $CaSO_4 \cdot 2H_2O$.

NOTE.—Chalk and other forms of alkaline earth carbonates are not determined by this method, but are considered under the determination of free alkalinity.

Determination of Soap.—The solution resulting from the decomposition of the filler-free grease or the combined filtrate and washes from the determination of fillers, except the alcohol, which is discarded, shall be placed in

a separator, allowed to clear, and the aqueous layer (*A*),[24] which contains all the bases as well as glycerin, shall be drawn into another separator. The

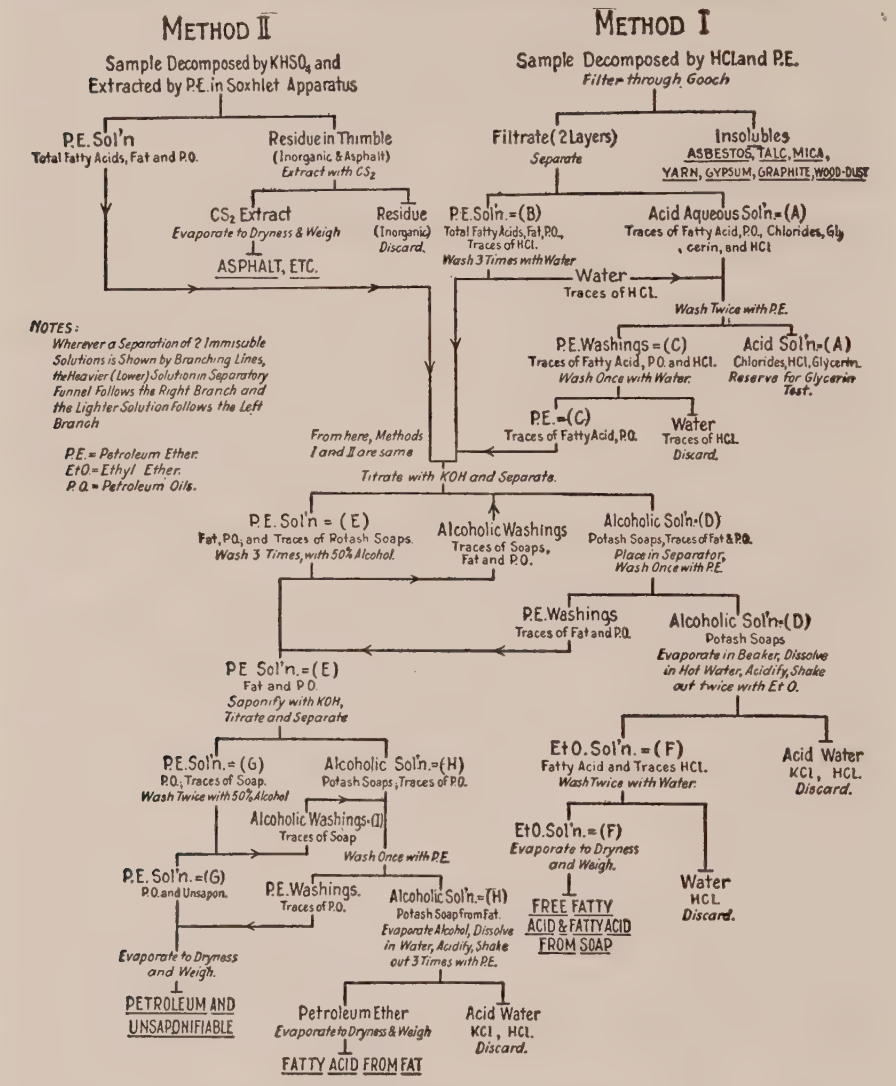
METHOD II
Sample Decomposed by KHSO4 and Extracted by P.E. in Soxhlet Apparatus
P.E. Sol'n
Total Fatty Acids, Fat and P.O.
Residue in Thimble
(Inorganic & Asphalt)
Extract with CS2
CS2 Extract
Evaporate to Dryness & Weigh
ASPHALT, ETC.
Residue
(Inorganic)
Discard.
METHOD I
Sample Decomposed by HCl and P.E.
Filter through Gooch
Filtrate (2 Layers)
Separate
Insolubles
ASBESTOS, TALC, MICA, YARN, GYPSUM, GRAPHITE, WOOD-DUST
P.E. Soln.=(B)
Total Fatty Acids, Fat, P.O., Traces of HCl.
Wash 3 Times with Water
Acid Aqueous Soln.=(A)
Traces of Fatty Acid, P.O., Chlorides, Glycerin, and HCl
Water
Traces of HCl.
Wash Twice with P.E.
NOTES:
Wherever a Separation of 2 Immisable Solutions is Shown by Branching Lines, the Heavier (Lower) Solution in Separatory Funnel Follows the Right Branch and the Lighter Solution Follows the Left Branch
P.E. = Petroleum Ether.
Et O = Ethyl Ether.
P.O. = Petroleum Oils.
P.E. Washings = (C)
Traces of Fatty Acid, P.O. and HCl.
Wash Once with Water.
Acid Soln.=(A)
Chlorides, HCl, Glycerin.
Reserve for Glycerin Test.
P.E.=(C)
Traces of Fatty Acid, P.O.
Water
Traces of HCl.
Discard.
From here, Methods I and II are same
Titrate with KOH and Separate.
P.E. Soln = (E)
Fat, P.O., and Traces of Potash Soaps.
Wash 3 Times, with 50% Alcohol.
Alcoholic Washings
Traces of Soaps, Fat and P.O.
Alcoholic Soln.=(D)
Potash Soaps, Traces of Fat & P.O.
Place in Separator, Wash Once with P.E.
P.E. Washings
Traces of Fat and P.O.
Alcoholic Soln.=(D)
Potash Soaps
Evaporate in Beaker, Dissolve in Hot Water, Acidify, Shake out twice with Et O.
P.E. Sol'n.=(E)
Fat and P.O.
Saponify with KOH, Titrate and Separate
Et O. Soln.=(F)
Fatty Acid and Traces HCl.
Wash Twice with Water.
Acid Water
KCl, HCl.
Discard.
P.E. Soln.=(G)
P.O., Traces of Soap.
Wash Twice with 50% Alcohol
Alcoholic Soln.=(H)
Potash Soaps, Traces of P.O.
Alcoholic Washings=(I)
Traces of Soap
Wash Once with P.E.
Et O. Soln.=(F)
Evaporate to Dryness and Weigh.
FREE FATTY ACID & FATTY ACID FROM SOAP
Water
HCl
Discard.
P.E. Soln.=(G)
P.O. and Unsapon.
P.E. Washings.
Traces of P.O.
Alcoholic Soln.=(H)
Potash Soap from Fat.
Evaporate Alcohol, Dissolve in Water, Acidify, Shake out 3 Times with P.E.
Evaporate to Dryness and Weigh.
PETROLEUM AND UNSAPONIFIABLE
Petroleum Ether
Evaporate to Dryness & Weigh
FATTY ACID FROM FAT
Acid Water
KCl, HCl.
Discard.

FIG. 264.—Scheme of Grease Analysis.

petroleum ether layer (*B*) shall be washed three times with 25 ml. of water to remove hydrochloric acid, adding the washings to (*A*). Solution (*B*) shall

[24] Solutions designated by capital letters in parentheses refer to the solutions given in Fig. 264.

then be run into a 250-ml. separator. The aqueous solution (*A*) shall then be washed twice with 20 ml. of petroleum ether (*C*), whereupon (*A*) is set aside for examination for glycerin. Solution (*C*) shall then be washed once with 15 ml. of water, which is rejected, and (*C*) shall be added to (*B*). If (*B*) and (*C*) are comparatively light colored, an approximate determination of free fatty acids and fatty acids from soap may now be made by titrating the solution in the separator with 0.5 N alcoholic potassium hydroxide and phenolphthalein, using 200 as the average neutralization value of the fatty acid (that is, 1.0 g. of fatty acid requires 200 mg. of absolute KOH for neutralization). If solutions (*B*) and (*C*) are dark, a few drops of phenolphthalein and sufficient 0.5 N alcoholic potassium hydroxide shall be added to make the alcoholic layer distinctly alkaline after vigorous shaking. If the solutions have been titrated, a slight excess of alkali shall be added before separating. The conservative addition of strong alcohol at this point may aid in securing rapid and sharp separation. The two solutions shall be allowed to separate sharply and the lower alcoholic layer (*D*) drawn off into another separator. The upper petroleum ether layer (*E*) shall be washed three times, with 30, 25 and 20 ml. of neutral 50% alcohol respectively, adding these washes to (*D*). Solution (*D*) shall be washed with 25 ml. of petroleum ether, after which (*D*) is drawn off into a beaker and the petroleum ether added to (*E*). Solution (*D*) shall then be evaporated to a small volume to remove alcohol, the residue of potassium soap washed into a separator with hot water, acidified with hydrochloric acid and shaken out twice with 50 and 25 ml. of ethyl ether (*F*), respectively. Solution (*F*) shall be run into another separator and washed twice with 20-ml. portions of water, which is discarded. Solution (*F*) shall then be transferred to a weighed beaker and evaporated to dryness on the steam bath, blowing with air to remove all traces of petroleum ether. The residue consisting of free fatty acid and fatty acid from soap shall be heated for a short time on a steam bath, adding and evaporating 5 ml. of absolute alcohol to remove the last traces of water, and weighed. The exact neutralization value shall then be determined on as large a sample of these fatty acids as possible. From the total fatty acid found here, the free acid if any (see Sections on Free Alkali and Free Acid) shall be deducted and the remainder calculated to percentage of soap, the ash analysis being used as a guide in distributing the bases, if more than one are present.

The fatty acids may be identified to some extent by special tests, such as odor, crystal form, melting point, iodine number, neutralization value, color reactions, etc.

If the grease is appreciably oxidized, the fatty acids obtained by the ethyl ether extraction are likely to be dark in color and hard to identify. For further study and identification, the neutralized acids may be extracted again (qualitatively) with petroleum ether and dilute HCl, thus eliminating the small amount of more darkly colored matter.

Detection of Glycerin.—In case it is desired to determine whether a grease has been made from whole fats or from fatty acids, solution (*A*) shall be neutralized with dry sodium carbonate and sufficient excess added to precipitate calcium or other metals. The whole mass shall then be evaporated to dryness, the residue extracted several times with strong alcohol, the combined alcoholic extracts filtered, and the alcohol evaporated. The residue will then contain

most of the glycerin, with a little sodium chloride. The presence or absence of glycerin in the residue shall be confirmed by suitable qualitative tests.

Since fats on saponification yield between 10 and 11% of glycerin, and this analytical scheme does not include a quantitative determination of glycerin, the total percentages in greases made from fats should always be less than 100.[25]

Determination of Fat.—The petroleum ether solution (*E*), containing free fat, petroleum oils, and unsaponifiable matter shall be concentrated to a volume of about 125 ml. in a 300-ml. Erlenmeyer flask, 10 ml. of 0.5 N alcoholic potassium hydroxide and 50 ml. of strong neutral alcohol added, and the whole boiled on a hot plate with an air condenser for 1½ hours. The uncombined alkali shall be titrated with 0.5 N hydrochloric acid, and from the alkali consumed, corrected for the blank determination as specified under Solvents, the percentage of free fat shall be calculated, using 195 as the average saponification value (that is, 1.0 g. of fat requires 195 mg. of absolute KOH for saponification).

The titrated solution (*G*) shall be placed in a separator, the alcoholic lower layer (*H*) drawn off into another separator and the remaining traces of soap removed as described for (*B*) and (*C*), Determination of Soap, making only two washes with 30 and 20 ml. of 50% alcohol (*I*). Solutions (*H*) and (*I*) shall be combined, washed once with a little petroleum ether, which is added to solution (*G*), and solutions (*H*) and (*I*) then evaporated to a small volume and the fatty acid isolated as described for (*D*), Determination of Soap. The percentage of fat may be checked by weighing and titrating the free fatty acid.[26]

Determination of Petroleum Oil.—The petroleum ether solution (*G*), now containing all the hydrocarbon oils and unsaponifiable matter shall be evaporated to dryness in a weighed beaker as described for (*F*), (**Soap**), the residue weighed, and the result reported as " petroleum oils plus unsaponifiable matter."

An approximate determination of the viscosity of the petroleum oil may be made by using a 2 or 5-ml. pipette which has been standardized against oils of known viscosities. If a complete characterization of the petroleum products is required, a new sample of from 150 to 200 g. of grease shall be decomposed as described above, except that all quantitative operations shall be omitted, as well as the isolation of the free fatty acids, and the use of standard alkali and acid is not necessary.

If the grease contains rosin oil, beeswax, degras, spermaceti, spermatin, montan wax, candle pitch, and other materials containing a large amount of unsaponifiable substances, the petroleum oils isolated from solution (*G*) will contain the unsaponifiable matter, and the constants found will differ from those of the petroleum products used in making the grease. In most cases, no further separation is possible except in the hands of skillful and experienced operators who can devise special methods to suit the individual conditions.

(2) *Determination of Filler, Soap, Fat, Etc.—Method for Dark Greases.*—The sample shall be weighed in a 3-in. porcelain dish, 10 g. of granulated acid

[25] A close approximation to the amount of glycerin present may be calculated and included in the analysis, by taking 11.0% of the weight of the fatty acids from soaps, providing, of course, that the grease was made from neutral fats.

[26] Multiplying the weight of fatty acid by 1.045 gives a very close approximation of the weight of fat from which it was derived. This factor varies very little with the molecular weight of the fat.

potassium sulfate added and 10 g. of clean dry ignited sand. The dish and contents shall be heated on the steam bath with frequent stirring until all water is driven off, two hours usually being sufficient. After cooling and breaking up lumps with a small pestle, the mixture shall be transferred quantitatively to an extraction thimble, using a little petroleum ether to wash the last traces into the thimble, which should be already placed in a Soxhlet apparatus. The thimble shall be extracted thoroughly with petroleum ether, the extract concentrated somewhat if necessary, and the free fatty acid and fatty acid from soap titrated with 0.5 N alcoholic potassium hydroxide as in solutions (*B*) and (*C*), in method (1), Determination of Soap. From this point on, the procedure is identical with that given in method (1), for soap, fat, and petroleum oil.

The thimble shall be extracted a second time with carbon disulfide, the extract evaporated to dryness, heated for one hour to 120° C. and weighed, the results being reported as asphaltic and tarry matter. The residue in the thimble shall be discarded.

(*E*) ***Determination of Free Alkali and Free Acid.***—From 10 to 30 g. of grease shall be weighed in a small beaker, dissolved as completely as possible in 75 ml. of petroleum ether by stirring with a spatula, the mixture washed into a 250-ml. Erlenmeyer flask with a small amount of petroleum ether, and the beaker rinsed with 50 ml. of 50% alcohol, the alcohol being poured into the flask, after which a few drops of phenolphthalein solution shall be added and the whole shaken vigorously. If the alcoholic layer, after settling for a few seconds, is pink, 10 ml. of 0.5 N hydrochloric acid shall be added, the solutions boiled on a hot plate for ten minutes to expel carbon dioxide, and the excess acid titrated back with 0.5 N alcoholic potassium hydroxide. The free alkalinity shall be calculated in terms of hydroxide of the predominating base.

Insoluble Carbonates.—If chalk or any other form of alkaline earth carbonate, or lead carbonate, is present as a filler, it will be detected by effervescence on adding the hydrochloric acid. As the amount of such carbonates is likely to be considerable, the volume of 0.5 N hydrochloric acid added shall be increased sufficiently to dissolve all carbonate and leave a slight excess of acid. The solution shall be boiled for two minutes and the excess acid titrated back with 0.5 N alcoholic potassium hydroxide, and from the acid consumed, its equivalent in calcium carbonate, etc., shall be calculated, disregarding any other forms of alkalinity which may have been present.

Free Acid.—If the original alcoholic layer is not pink, the solution shall be titrated carefully in the cold with 0.5 N alcoholic potassium hydroxide, shaking well after each addition. The acidity shall be calculated as oleic acid.

If soaps of iron, zinc, aluminum, or other weak bases are present, a determination of free acid is not possible, since these metallic soaps react with potassium hydroxide. Up to the present, no means has been devised whereby this determination can be made directly.

(*F*) ***Determination of Water.***—The quantity of water shall be determined in accordance with the Standard Method of Test for Water in Petroleum Products and Other Bituminous Materials (A. S. T. M. Designation: D 95) of the American Society for Testing Materials.[27]

[27] 1933 Book of A. S. T. M. Standards, Part II, p. 891.

Waxes

The melting point of mineral waxes may indicate its origin and determines its classification. A wide range of temperature in the melting shows a mixture of waxes and incomplete refining methods.

STANDARD METHOD OF TEST FOR MELTING POINT OF PARAFFIN WAX[28]

A. S. T. M. Designation: D 87–22[29]

Definition.—***A. S. T. M. Paraffin Wax Melting Point.***—The A. S. T. M. Paraffin Wax Melting Point is the temperature at which melted paraffin wax, when allowed to cool under definite prescribed conditions, first shows a minimum rate of temperature change.

Note.—The so-called "American Melting Point" is an arbritary figure 3° F. higher than the A. S. T. M. Paraffin Wax Melting Point.

Apparatus.—***Wax Container.***—Test tube of standard form, 25 mm. (1 in.) outside diameter and 100 mm. (4 in.) long. It may be marked with a filling line, 2 in. above the bottom. This test tube shall be closed in a tightly fitting cork having two openings, one at the center for the melting point thermometer and the other for a stirrer at one side of the center. The opening for the stirrer may be lined with glass or metal tubing to act as a guide for the stirrer.

Air Bath.—Suitable water-tight cylinder, 2 in. in inside diameter and 4½ in. deep. This air bath shall be provided with a tightly fitting cork having a central opening for holding the test tube firmly in a vertical position in the center of the air bath.

Water Bath.—Suitable cylinder, 5⅛ in. in inside diameter and 6 in. deep. This water bath shall be provided with a suitable cover and with the guides and fasteners necessary to hold the air bath firmly in a vertical central position so that the sides and bottom of the air bath shall be surrounded by a layer of water 1½ in. thick. The water bath cover shall have a slot for introduction of a suitable stirrer and shall have an opening for the bath thermometer so that the latter may be suspended in a vertical position ¾ in. from the outside wall of the water bath. Air bath, water bath and water bath cover may be conveniently made of metal in one assembly as shown in Fig. 264.

Stirrer in Test Tube.—Brass or copper wire, ⅛ in. in diameter and about 12 in. long. A circular loop, ½ in. in diameter, shall be formed at one end of this wire in such a manner that the loop lies in a horizontal plane when the rest of the wire is in a vertical position. The stirrer thus formed shall be passed through the proper opening in the test-tube cork and the upper end may then be bent into a shape convenient for holding.

[28] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[29] This method is issued under the fixed designation D 87; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1921; Adopted, 1922. This method has been approved as American Standard by the American Standards Association.

Thermometer.—The A. S. T. M. Paraffin Wax Melting Point thermometer shall conform to the following requirements. These specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being 27 to 71° C. or 80 to 160° F., respectively.

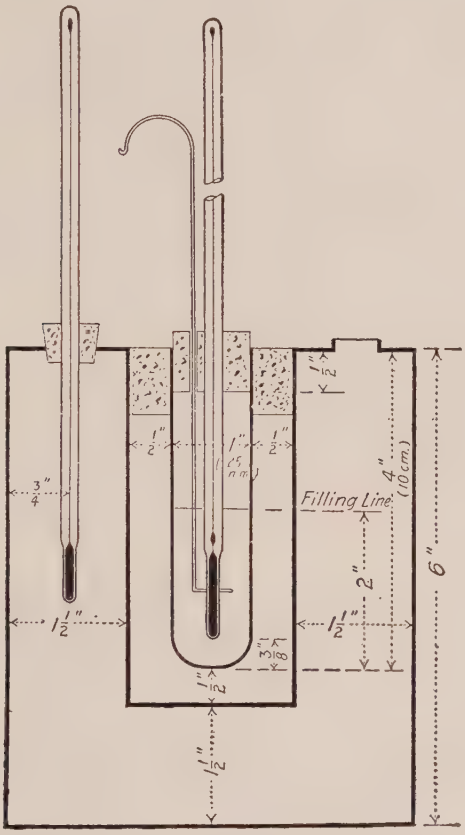

Fig. 264a.—Apparatus for Determination of Melting Point of Paraffin Wax.

Type: Etched stem, glass.
Liquid: Mercury.
Range and Subdivision: 27 to 71° C. in 0.1° C. or 80 to 160° F. in 0.2° F.
Total Length: 365 to 371 mm. (14.38 to 14.56 in.).
Stem: Plain front, enamel back, suitable thermometer tubing. Diameter, 6.0 to 7.0 mm. (0.24 to 0.28 in.).
Bulb: Corning normal or equally suitable thermometric glass.
Length, not over 28 mm. (1.10 in.).
Diameter, not greater than stem.
Distance to 27° C. or 80° F. Line from Bottom of Bulb: 105 to 115 mm. (4.13 to 4.53 in.).
Distance to 71° C. or 160° F. Line from Top of Thermometer: 25 to 40 mm. (0.98 to 1.57 in.).

CONTRACTION CHAMBER: Top to be not more than 41 mm. (1.61 in.) above bottom of bulb.
EXPANSION CHAMBER: To permit heating the thermometer to at least 100° C. (212° F.).
FILLING ABOVE MERCURY: Nitrogen gas.
TOP FINISH: Plain.
GRADUATION: All lines, figures, and letters clear cut and distinct. The first and each succeeding fifth line to be longer than the remaining lines. Graduations to be numbered at each 1° C. or each multiple of 2° F.
IMMERSION: 79 mm. or 3⅛ in. The words "79-mm. immersion" on Centigrade thermometers or "3⅛-in. immersion" on Fahrenheit thermometers, and a line around the stem 79.0 mm. or 3.13 in. above the bottom of the bulb shall be etched on the stem.
SPECIAL MARKING: "A. S. T. M. Pffe. M.P.," a serial number and the manufacturer's name or trade mark shall be etched on the stem.
SCALE ERROR: The error at any point of the scale when the thermometer is standardized as provided below shall not exceed 0.1° C. or 0.2° F., respectively.
STANDARDIZATION: The thermometer shall be standardized at intervals of approximately 10° C. or 20° F. for 79-mm. or 3 ⅛-in. immersion and for an average temperature of the emergent mercury column of 25° C. or 77° F.
CASE: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A. S. T. M. Pffe. M.P., 27 to 71° C." or "A. S. T. M. Pffe. M.P., 80 to 160° F." according to the type of thermometer.

NOTE.—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.
The diameter is that measured with a ring gage.
The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.
The top of the thermometer is the top of the finished instrument.

Bath thermometer of any suitable type, accurate to 2° F. throughout the required range.

Procedure.—An average sample of the wax to be tested shall be melted in a suitable container in a water bath whose temperature shall be not more than 35° F. above the approximate melting point of the wax sample. Direct heat, such as a flame or hot plate, shall not be used and the wax sample shall not be held in the melted condition any longer than necessary.

The test tube shall be filled with melted wax to a height of 2 in. The test-tube cork, carrying the stirrer and the melting point thermometer with the 3⅛-in. immersion line at the under surface of the cork, shall be inserted into the test tube for a distance of ½ in. The lower end of the thermometer bulb shall then be ⅜ in. from the bottom of the test tube.

The air bath being in its proper position in the water bath, the latter shall be filled to within ½ in. of the top with water at a temperature 15 to 20° F. below the approximate melting point of the wax sample.

The test tube containing the melted wax, with wax stirrer and thermometer in place, shall be inserted into the air bath in a central vertical position so that the bottom of the test tube is ½ in. from the bottom of the air bath. The temperature of the water bath shall be adjusted by stirring if necessary, so that it shall be lower than the temperature of the wax sample by not more than 30° F. and not less than 25° F., when the wax sample has cooled to a temperature 10° F. above its approximate melting point.

When these conditions have been obtained, temperature adjustment and stirring of the water bath shall be discontinued. The wax shall be stirred continuously during the remainder of the test, the stirring loop being moved

up and down throughout the entire length of the test tube in a steady motion at the rate of 20 complete cycles per minute. The melting point thermometer reading, estimated to 0.1° F. shall be observed and recorded every 30 seconds. The temperature of the wax will fall gradually at first, will then become almost constant and will then again fall gradually.

The melting point thermometer reading, estimated to 0.1° F., shall be observed and recorded every 30 seconds, for at least three minutes after the temperature again begins to fall after remaining almost constant. The record of temperature readings shall then be inspected and the average of the first four readings that lie within a range of 0.2° F. shall be considered as the uncorrected melting point. This temperature shall be corrected if necessary for error in the thermometer scale and the corrected temperature shall be reported as the " A. S. T. M. Paraffin Wax Melting Point."

Accuracy.—Duplicate determinations on the same sample should differ by not more than 0.2° F.

Heavy Oils and Asphalts

The heavy oils may be crude oils with a low Baumé gravity or residues from the distillation of mixed or asphaltic base crudes. They are used for fuel oil, dust laying oils and road oils. Asphalts may be found in nature in a semi-liquid (Baumé gravity 10) or a mixture of sand and limestone. Artificial asphalts are the residues of asphaltic base crude oils and may be polymerized into a hard asphalt by blowing air through the residues at high temperatures.

See the chapter on Bituminous Substances for methods of testing emulsified Asphalts.

The testing of **fuel oils** is of little value unless the specifications for the individual oil are given. The many types of burners and the various conditions under which fuel oils are used make any one set of specifications impossible to use. The term fuel oil as now used is broad in meaning and may range from a mineral seal distillate to heavy residues or a mixture of oils having no other apparent use.

The gravity of fuel oils gives little information unless other information is obtainable. The flash point is important and should be higher than the temperature at which the oil is sufficiently fluid for the particular apparatus for which it is desired. A low flash shows a naphtha and should not be used in open burners. The viscosity of an oil must be low enough so that it will flow readily at low temperatures. Water and sediment (page 1761) choke the burners and freeze in the pipes during low temperatures. The fuel [30] should not contain grit, acid, fibrous or other foreign matter and shall pass through a filter of wire gauze 16 meshes to the inch.

The sulfur content when high (over 2.5%) indicates a residue of a high sulfur crude or a mixture of fuels obtained from acid recovery plants. A high sulfur fuel causes rapid corrosion of all exposed metal parts of stills and boilers.

[30] U. S. Bureau of Mines Bulletin 323A.

STANDARD METHOD OF TEST FOR THERMAL VALUE OF FUEL OIL [31]

A. S. T. M. Designation: D 240–27 [32]

Apparatus.—***Combustion Bombs.***—The Atwater, Davis, Emerson, Mahler, Parr, Peters, Williams or similar bombs may be used. The bomb shall have an inner surface of platinum, gold, porcelain enamel or other material which is not attacked by nitric and sulfuric acids, or other products of combustion.

Calorimeter Jacket.—The calorimeter shall be provided with a vacuum jacket or with a water jacket having a cover to protect the calorimeter from air currents. In case a water jacket is used, it shall be kept filled with water within 2 or 3° C. of the temperature of the room (except in calorimeters which are totally submerged, where the jacket temperature is controlled by a thermostat) and this water should be stirred continuously by some mechanical stirring device.

Stirring of the Calorimeter Water.—The water in the calorimeter shall be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. A motor-driven screw or turbine stirrer is recommended and the speed should not be excessive. This may be determined by adjusting the temperature of the calorimeter to equality with that of the jacket and allowing the stirrer to run continuously for 10 minutes. If the temperature of the calorimeter rises more than about 0.01° C. in this length of time, the rate of stirring is excessive. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is irregular. The portion of the stirring device immersed in the calorimeter should be separated from that outside by non-conducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

Thermometers.—The thermometers used shall have been certified by a government testing bureau and shall be used with the corrections given on the certificate. This shall also apply to electrical resistance or thermo-electric thermometers. Correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the " setting " of Beckmann thermometers. For accurate work, either Beckmann or special calorimetric thermometers, graduated to 0.01 or 0.02° C., are required. Such thermometers should be tapped lightly just before each reading to avoid errors caused by the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

[31] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Reproduced through the courtesy of the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

[32] This method is issued under the fixed designation D 240; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision. Issued as Tentative, 1926; Adopted in Amended Form, 1927. This method has been approved as American Standard by the American Standards Association.

Oxygen.—The oxygen used for combustions shall be free from combustible material. The bomb when filled should contain at least 5% of nitrogen to insure complete oxidation of the sulfur. The total amount of oxygen contained in the bomb for combustion shall be not less than 5 g. per gram of fuel oil. But the combustion must be complete, as shown by the absence of any sooty deposit on opening the bomb after firing.

Firing Wire.—The fuel oil in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used, it should be of about No. 34 B. & S. gage and not more than 10 cm. (preferably 5 cm.) should be used at a time. A correction of 1600 calories per gram weight of iron wire burned shall be subtracted from the observed number of calories.

Standardization.—The water equivalent of a calorimeter can best be determined by the use of the standard combustion samples supplied by the U. S. Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of standard samples supplied by the Bureau of Standards, and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of each of two of the standard materials which are, sucrose, naphthalene and benzoic acid. The conditions as to the amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made, shall be the same as for fuel oil combustions. In the case of any disagreement between contracting parties a check standardization may consist of two or more combustions of standardizing samples.

Procedure.—***Preparation of Sample.***—Approximately enough oil shall be taken to give a thermometer rise of from 3° to 4° C. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation in the use of naphthalene for standardization.

Preparation of the Bomb.—The firing wire, if iron, shall be measured and coiled in a small spiral and connected between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire to make the connection. The platinum and the iron shall both be clean. About 0.5 ml. of water should be placed in the bottom of the bomb to saturate with moisture the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the fuel oil or briquet of standard material. For the combustion of standardizing samples, iron wire is preferable to platinum.

Filling the Bomb with Oxygen.—Oxygen from the supply tank shall be admitted slowly, to avoid blowing the oil from the crucible, until a pressure is reached as indicated by the following table:

Capacity of Bomb, ml.	Minimum Gage Pressure, Atmospheres
300 to 350	40
350 to 400	35
400 to 450	30
450 to 500	27.5
Above 500	25

Calorimeter Water.—The calorimeter shall be filled with the required amount of distilled water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standardized flask or by weighing. The amount shall be kept the same as that used in the standardization of the apparatus.

Temperature Adjustments.—The initial temperature in the calorimeter shall be so adjusted that the final temperature, after the combustion, will not be more than 1° C., preferably about 0.5° C., above that of the jacket. Under these conditions, the total correction for heat gained from or lost to the surroundings will be small when the rise of temperature is 3° or 4° C. and the effect of evaporation will also be small.

Firing Current.—The electric current used for firing the charge shall be obtained from storage or dry cells having an electromotive force of not more than 12 volts. A higher voltage is liable to cause an arc between the firing terminals, introducing additional heat which cannot be measured with certainty. The circuit should be closed by means of a switch which should remain closed for not more than 2 seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out.

Method of Making an Observation.—The bomb, when ready for firing, shall be placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer shall then be started and after the thermometer reading has become steady, not less than 2 minutes after the stirrer is started, the temperatures shall be read at 1-minute intervals for 5 minutes and the charge then fired, the exact time of firing being noted. Observations of temperature shall then be made at intervals depending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings shall be taken at 1-minute intervals for 5 minutes to determine the final cooling rate.

Titration.—After a combustion and after allowing the gas to escape, the bomb shall be opened and the inside examined for traces of unburned material or sooty deposit. If these are found, the observations shall be discarded. If the combustion appears complete, the bomb shall be rinsed out thoroughly and the washings titrated with a standard alkali solution (1 ml. = 0.02173 g. HNO_3 = 5 calories) using methyl-orange or methyl-red indicator to determine the amount of acid formed. A correction of 230 calories per gram of HNO_3 should be subtracted from the total heat observed. An additional correction of 1300 calories per gram of sulfur in the oil should be made for the excess of difference in heats of formation of SO_2 and aqueous H_2SO_4 over the heat of formation of aqueous HNO_3.

Computation of Results.—The following method of computation is recommended to take the place of the Pfaundler or other similar formulas for computing the cooling correction (radiation correction):

Observe (1) the rate of rise, r_1, of the calorimeter temperature in degrees per minute for 5 minutes before firing; (2) the time, a, at which the last temperature reading is made immediately before firing; (3) the time, b, when the rise of temperature has reached six-tenths of its total amount (this point can

generally be determined by adding to the temperature observed before firing, 60% of the expected temperature rise, and noting the time at which this point is reached); (4) the time, c, of a thermometer reading taken when the temperature change has become uniform some 5 minutes after firing; (5) the final rate of cooling, r_2, in degrees per minute for 5 minutes.

Multiply the rate r_1 by the time $b-a$ in minutes and tenths of a minute, and add to this product (subtracted if the temperature was falling at the time a) to the thermometer reading taken at the time a. Multiply the rate r_2 by the time $c-b$ and add this product (subtracted if the temperature was rising at the time c and later) to the thermometer reading taken at the time c. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This, multiplied by the water equivalent of the calorimeter, gives the total amount of heat liberated. Divide this result, corrected for the heats of formation of HNO_3 and H_2SO_4 observed and for the heat of combustion of the firing wire, when that is included, by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the British thermal units per pound.

The permissible difference between duplicate determinations made by different analysts on different calorimeters shall not exceed 0.5%. When made by the same analyst on the same calorimeter, the permissible difference shall not exceed 0.3%.

In practice, the time $b-a$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

The results shall be reduced to calories per gram or British thermal units per pound of oil.

Road Oils

Road oils may be used as dust-laying oils, binders for sand, sandy loam and gravel roads. The value of a road oil depends upon its penetration into the soil, the binding qualities of the oil, and its resistance to weather and wear.

The tests on road oils are important in as much as the importance of the specifications for the particular duty for which they are intended. Road oils are often placed on roads without any study as to the adaptability of the oil for the soil or base on which it is placed.

Gravity is a common test made on road oils but has little value. The asphalt in a road oil acts as the binder and weather-resisting element. The total bitumen (page 1539) is determined to give the value of the oil as a binder. The penetration of the asphalt into the road bed determines its wearing qualities. The viscosity should be low enough to enable to penetrate the soil and to flow with ease and uniformly when applied. A heavy asphalt oil mixed with a lighter oil will give greater penetration, the lighter oil slowly evaporating, leaving a layer of high asphaltic content in the soil. The asphalt should contain little or no paraffin wax. The wax particles combine with the soil and form little dry particles which soon wear loose and blow away leaving small pits in the surface which soon wear away forming large holes and ruts in the finished roads.

Asphalts either native or artificial when used for paving should be tested for total bitumen, penetration (page 1520), viscosity (page 1518) and carbene (page 1546) content. If asphalts are made from petroleum residues, the wax content should be determined. Petroleum with a carbene content over .5% (part insoluble in carbon tetrachloride) indicates that the residue had been overheated or overblown, making a brittle product.

Shale Oils

The testing of shale oils is much the same as the testing of petroleums. Shale oils are made by the retorting of the oil shales changing the pyrobitumens into the bitumens. The bitumens formed vary in chemical and physical properties as the methods of retorting. High temperatures cause " cracking " with a resulting polymerization. The nitrogen and sulfur content being high gives a different reaction to heat than petroleums of the same gravity.

The waxes made from shales have a higher melting point than the paraffin from petroleum. They may be separated into a white flake wax by washing the re-run lubricating distillate with acetone. This method can be used as a quantitative test for waxes in shale oils.

The different finished products, gasolines, kerosenes, fuel oils, lubricants and waxes, are tested in the same manner as similar petroleum products.

ANALYSIS OF PAINTS

In reporting the results of an examination of a paint, it is advisable to give all the analytical data as well as a résumé showing the probable composition of the paint. This is shown in the following example:

RESULTS OF ANALYSIS

Total Pigments or Solids	60%
Total Vehicle or Liquids	40

Analysis of Pigment Portion

Lead Oxide (PbO)	37.47%
Zinc Oxide (ZnO)	44.50
Alumina, iron, lime	2.90
Magnesia (MgO)	1.90
Silica (SiO_2)	4.63
Carbon Dioxide (CO_2)	2.50
Sulfuric Anhydride (SO_3)	5.02
Water (combined)	.73
	99.15%

Analysis of Liquid Portion

Vehicle contained 20% volatile matter.
Volatile matter consisted of equal parts of turpentine and mineral spirits.
Non-volatile matter had:

Iodine Number	175
Acid Number	2.4
Saponification Number	188

and contained .02% ash consisting of lead and manganese oxides.

Probable Composition of Paint

Pigment	60%
Liquid	40

Pigment

Basic carbonate White lead	22%
Basic sulfate White lead	25
Zinc Oxide	43
Asbestine	10
	100%

Liquid

Raw Linseed Oil	80%
Mineral Spirits	10
Turpentine and Drier	10
	100%

Chapter contributed by Henry A. Gardner, John A. Schaeffer and G. G. Sward.

SEPARATION OF PIGMENT AND LIQUID

Composition of Liquid Part.—The vehicle or liquid portion of paints may contain various fixed animal, vegetable or mineral oils, oleo-resinous varnishes, turpentine, petroleum distillates, and driers.

It is always advisable to determine the total percentage of liquids in a paint. The container should be thoroughly shaken so that the contents will be uniform throughout. A portion of 4 or 5 ounces may then be removed and placed in a screw-cap bottle. The original can of paint should then be set aside so that settling of the pigments will take place. Unless the paint is in paste form, this will usually be accomplished in twenty-four hours. A portion of the clear liquid floating over the pigments may then be removed and directly examined as outlined under Separation of Vehicle Components.

Percentage of Liquid by Ignition Method.—The percentage of liquid in the uniform sample of paint previously obtained may be found by placing a weighed portion in a porcelain crucible and slowly igniting it to burn off the organic constituents. By carefully regulating the heat, the oil and volatile thinners will be slowly burned off, leaving the pigment behind, which may then be weighed, calculating the vehicle by difference. This method is rapid and works well with pigments that are not decomposed by the ignition. When pigments are present which show an appreciable loss on ignition, or blacks or blues, this method is not to be relied upon.

Percentage of Liquid by Extraction Methods.—From 10 to 20 grams of paint is placed in a 100-ml. weighed centrifuge tube, the exact amount being obtained by difference. The paint is thinned with a suitable extraction liquid and centrifuged. The supernatant liquid is then poured off and the process repeated two or three times. The pigment is then dried, first in air, and finally in an oven. The tube and pigment are weighed and the percentage of vehicle obtained by difference.

In case a centrifuge is not available, the vehicle of many paints may be separated by simply shaking a portion of the paint in a long test-tube with the extraction liquid, allowing the pigment to settle, repeating the extraction until the oil is thoroughly removed.

Some operators use a Soxhlet extractor for the determination of the vehicle of a paint. This method is rather slow and does not always give satisfactory results.

It must be remembered that no method of extraction of the oil from a paint will give absolute results. The last traces of oil cannot be removed from the pigment, which is probably due to the fact that many pigments such as lead and zinc react with the oil, producing small quantities of insoluble soaps which are not completely dissolved by the solvent.

The choice of a solvent is important. For linseed oil paints, diethyl ether, petroleum ether, benzene, and other solvents for the oil are suitable. If varnish is present, some experimental work on various solvents may be necessary.

There are some pigments which by reason of their low specific gravity, colloidal nature or partial solubility can never be completely separated from oil, either by settling, centrifuging or extraction. Of these the most commonly met with are lampblack and other forms of carbon, zinc oxide and Prussian

blue. Colloidal pigments such as zinc oxide are very troublesome in this respect. When these pigments, however, are present in a paint in considerable percentage, the difficulty of their separation may be avoided by adding to the paint three or four times its volume of fuller's earth, diluting the mixture in a large test-tube with gasoline or petroleum ether and either centrifuging or placing in a rack to settle. The fuller's earth carries down the colloidal pigments and the separation is sharp and easy. This method, of course, is simply used to extract the vehicle present. The pigment resulting from the separation cannot be used for analysis on account of admixture with the fuller's earth.

In some cases the pigments in paste colors made of lampblack and Prussian blue cannot be separated from the liquid portion. The amount of Prussian blue present, however, may be determined by making a Kjeldahl-Gunning determination on a portion of the entire paint, multiplying the nitrogen found by 4.4. For the determination of the lampblack present, a portion of the entire paint may be boiled with an excess of alcoholic potash until all of the oil is saponified. The mixture is then decanted through a filter and washed, first with hot alcohol and then with hot water. This affords a very good separation of the liquid from the pigment of such paints. By this method, the Prussian blue which may be present is partially destroyed, the iron content remaining admixed with the black pigment on the filter.

Separation of Liquid Components.—Whenever possible, it is advisable to determine the constituents of the vehicle upon the sample that has been removed from the top of the settled can of paint. A weighed portion of this vehicle may be placed in a tared flask and attached to a Liebig condenser. Heating to 180° C. or lower will drive off nearly all the volatile constituents. The composition of the distillate may be determined by the methods given under the Examination of Turpentine. A portion of the residue in the flask, which consists of oil, driers, gums, etc., may be transferred to a crucible and ignited. The residue may then be weighed and calculated to ash. The ash should be analyzed for lead, manganese and other driers.

Another portion of the original vehicle may be evaporated in an atmosphere of CO_2 (prevents oxidation) to remove the volatile constituents. A portion of the oil residue may then be examined for iodine number and other constants. In most instances it would be advisable to make a saponification and extraction of the fatty acids from this residue, determining the iodine number on the fatty acids.

Water is best determined by distillation of the paint with a non-miscible liquid such as toluene. The distillate is collected in a graduated cylinder, the water settling to the bottom. A better way is to use the apparatus described by Dean and Stark.[1]

Direct Distillation for Volatiles.—For a direct determination of the volatile constituents in a paint, a sample may be distilled *in vacuo*. This is easily managed wherever a vacuum pump is available and avoids the necessity of overheating the oil. If, in order to obtain the fixed oils for analysis, a sample of the clear vehicle from a settled paint is used, it should not be heated above 150° C. and neither should the solvent be volatilized in such a way as to allow the oil to be in contact with air, as the oil will oxidize rapidly while warm and

[1] Ind. & Eng. Chem., **12**, 486 (1920). See p. 1340.

its iodine number be very much lowered. The volatile matter may also be separated by steam distillation.

Detection of Resinates.—To determine whether the drier in a paint is of the resinate type or linoleate type, a few drops of the oil liquid may be mixed on a porcelain plate with one or two drops of acetic anhydride, subsequently adding a drop of sulfuric acid. Upon the addition of the sulfuric acid, a flash of purple color, turning to dark brown, will be shown where rosin is present. This test is not conclusive and experience is necessary for its proper interpretation. If rosin should be present in the vehicle to a considerable extent, the oil will have a very high acid number. The approximate percentage of rosin present may be determined by shaking a portion of the vehicle with 95% alcohol in a separatory funnel, subsequently separating the alcoholic extract, evaporating and weighing the residue.

Detection of Various Oils.—Tung (Chinese wood oil) may be detected in the vehicle by mixing the oil with an equal volume of a saturated solution of iodine in petroleum ether, allowing the mixture to stand in direct sunlight. Under these conditions, a peculiar, insoluble, spongy polymer of one of the glycerides of Chinese wood oil is shown. Fish oil can sometimes be detected by its odor and the dark red color during saponification, but the best method is probably that of Eisenschiml and Copthorne [2] which depends upon the formation of insoluble bromine derivatives of the oil. The presence of soybean and other vegetable oils is in some cases difficult to detect. The iodine numbers of these oils, however, are all lower than that of linseed oil. It must be remembered, however, that the iodine number of boiled linseed oil is lower than that of raw oil and that the iodine number of oils extracted from many paints is usually lower than shown by the original oil. In the presence of considerable quantities of drier, it is always advisable to extract the fatty acids from oil and make the iodine number determination upon them.

Detection of Various Thinners.—The distillate from the paint vehicle may consist of turpentine, mineral distillates, benzol and similar solvents. The presence of benzol is readily detected by adding a few drops of the distillate to a small quantity of a mixture of concentrated nitric and sulfuric acids. Upon heating this mixture, the characteristic odor of nitro-benzol will be recognized if benzol is present. Mineral distillates from petroleum are easily detected by the polymerization method given under the Examination of Turpentine.

ANALYSIS OF PAINT OILS

Although linseed oil is used to the greatest extent in paints, some other oils occasionally find application in the manufacture of special paints. The following have been used for this purpose: soybean oil, perilla oil, corn oil, cottonseed oil, sunflower oil, lumbang oil and similar vegetable oils; menhaden

[2] Ind. Eng. Chem., 2, 28 (1910).

oil, whale oil, herring oil, and similar marine animal oils of relatively high iodine number.

There are given below specifications for, and methods for. the analysis of linseed oil, in accordance with the latest practice developed by the Federal Specifications Board of the Procurement Division of the U. S. Treasury Department. These methods may be followed in examining any of the other oils mentioned above.

Raw Linseed Oil

	Maximum	Minimum
Foots:		
Heated oil, per cent by volume	1.0	—
Chilled oil, per cent by volume	4.0	—
Specific gravity 15.5/15.5° C.	.936	0.931
Acid number	4.0	—
Saponification number	195.0	189.0
Unsaponifiable matter, per cent	1.50	—
Iodine number,[a] Wijs	—	177.0
Loss on heating at 105° to 110° C., per cent	.2	—
Color	[b]	[b]

[a] When high iodine number type of raw linseed oil is specified by the purchaser, the iodine number must be not less than 188 and the oil shall conform to all of the other requirements.

[b] Not darker than a freshly prepared solution of 1.0 g. potassium bichromate in 100 ml. pure concentrated sulfuric acid (sp.gr. 1.84).

Boiled Linseed Oil

	Maximum	Minimum
Time of drying on glass, hours	18.0	—
Loss on heating at 105° to 110° C., per cent	.2	—
Specific gravity at 15.5/15.5° C.	.945	0.937[a]
Acid number	7.5	—
Saponification number	195.0	189.0
Unsaponifiable matter, per cent	1.50	—
Iodine number, Wijs	—	170.0
Ash, per cent	.50	—
Lead, per cent	—	.05

[a] When quick process, not kettle-boiled, oil is called for in contract, the minimum specific gravity shall be 0.931.

Analysis of Linseed Oil

Loss on Heating at 105° to 110° C.—Place 10 grams of the oil in an accurately weighed 100-ml. Erlenmeyer flask; weigh. Heat in an oven at a temperature between 105 and 110° C. for 30 minutes; cool and weigh. Calculate the percentage loss. Make this determination in a current of dry carbon dioxide gas.

Foots General Test.—With all materials at a temperature between 20° and 27° C., mix, by shaking for exactly one minute in a graduated tube, 25 ml.

of the well-shaken sample of oil, 25 ml. of acetone, and 10 ml. of acid calcium chloride solution. Then clamp the tube in an upright position and allow to settle for 24 hours. The temperature during this period should be between 20° and 27° C. The graduated tube shall be of not less than 70 ml. capacity and shall have at least 50 ml. graduated in 0.1 ml. The diameter of the tube shall be such that the 50 ml. graduated portion shall be not less than 40 cm. or more than 60 cm. in length. The volume of the stratum lying between the clear calcium chloride solution and the clear acetone and oil mixture is read to 0.1 ml. or fraction thereof. This reading multiplied by four expresses the amount of foots present as percentage by volume of the oil taken.

Heated Oil.—Heat a portion of the oil to 65° C., hold it within 2° C. of that temperature for 10 minutes, then cool it to room temperature (20° to 27° C.). Promptly make the general foots test as described above.

Chilled Oil.—Heat a portion of the oil to 65° C., hold it within 2° C. of that temperature for 10 minutes, then place it in a clean, dry bottle, stopper tightly, and place in a cracked ice and water mixture (0° C.) for exactly two hours. At the end of this time place the bottle in a large bath of water at 25° C. and keep it there for 30 minutes, then promptly make the general foots test as described above.

Specific Gravity.—Determine at 15.5/15.5° C. by any convenient method that is accurate within two points in the fourth decimal place.

Acid Number.—Transfer 5 to 10 grams of the oil to a 300-ml. Erlenmeyer flask. Add 50 ml. of a mixture of equal parts by volume of 95% ethyl alcohol and chemically pure reagent benzol. (This mixture should be previously titrated to a very faint pink with dilute alkali solution, using phenolphthalein as an indicator.) Add phenolphthalein indicator and titrate at once to a faint permanent pink color with standard sodium or potassium hydroxide solution. Calculate the acid number (milligrams KOH per gram of oil).

Saponification Number.—Weigh about 2 grams of the oil in a 300-ml. Erlenmeyer flask. Add 25 ml. alcoholic sodium hydroxide solution. Put a condenser loop inside the neck of the flask and heat on the steam bath for one hour. Cool, add phenolphthalein as indicator, and titrate with half normal sulfuric acid. Run two blanks with the alcoholic sodium hydroxide solution. These should check within 0.1 ml. N/2 H_2SO_4. From the difference between the number of cubic centimeters of N/2 H_2SO_4 required for the blank and for the determination, calculate the saponification number (milligrams KOH required for 1 gram of oil).

Unsaponifiable Matter.—Transfer 8 to 10 grams of the oil to a 250-ml. long-neck flask. Add 5 cc. of strong solution of sodium hydroxide (equal weights of NaOH and H_2O), and 50 ml. 95% ethyl alcohol. Put a condenser loop inside the neck of the flask and boil for two hours. Occasionally agitate the flask to break up the liquid but do not project the liquid onto the sides of the flask. At the end of two hours remove the condenser and allow the liquid to boil down to about 25 ml.

Transfer to a 500-ml. glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 ml., add 100 ml. redistilled ether. Stopper and shake for one minute. Let stand until the two layers separate sharp and clear. Draw all but one or two drops of the aqueous layer into a second 500-ml. separatory funnel and repeat the process using 60 ml. of ether. After thorough

separation draw off the aqueous solution into a 400-ml. beaker, then the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel and shake out again with 60 ml. of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel.

Shake the combined ether solution with the accumulated water rinsings and let the layers separate sharp and clear. Draw off the water and add it to the main aqueous solution. Shake the ether solution with two portions of water (about 25 ml. each). Add these to the main water solution.

Swirl the separatory funnel so as to bring the last drops of water down to the stopcock, and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise if necessary) into a 250-ml. flask and distill off. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool and weigh. (*The unsaponifiable oil from adulterated drying oils is volatile and will evaporate on long heating. Therefore heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of ether is gone.*)

Iodine Number.—Place a small quantity of the sample in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.12 grams (0.09–0.15 grams) to a 500-ml. bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 ml. of chloroform. Whirl the bottle to dissolve the sample. Add 10 ml. of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 ml. of Wijs solution and let stand with occasional shaking for one hour. Add 10 ml. of the 15% potassium iodide solution and 100 ml. of water, and titrate with standard sodium thiosulfate using starch as indicator.

The titrations on the two blank tests should agree within 0.1 ml. From the difference between the average of the blank titration and the titration on the samples and the iodine value of the thiosulfate solution, calculate the iodine number of the samples tested. (Iodine number is centigrams of iodine to 1 gram of sample.)

Ash.—Tare a porcelain crucible or dish. Add 10 to 25 ml. of oil, weighing the amount added. Place on a stone slab on the floor of a hood. Ignite by playing the flame of a burner on the surface of the oil and allow to burn quietly until most of the oil is burned off; then transfer to a muffle or over a flame and continue heating at a very low temperature (not over a dull red) until all carbonaceous matter is consumed. Cool, weigh, and calculate the percentage of ash.

Driers.—Moisten the ash with a few drops of water and test with litmus paper. Record whether neutral or alkaline. Wash any ash adhering to the test paper back into the crucible. Dissolve the ash in dilute nitric acid to which a little hydrogen peroxide has been added. After solution is complete make up the volume to about 50 ml. with nitric acid and water so that the final volume will contain about 1 volume of concentrated nitric acid and 3 volumes of water. Boil to remove excess of hydrogen peroxide. Determine manganese by the bismuthate method. See Chapter on Manganese, Vol. I.

Ash another portion of the oil and dissolve the ash as above in nitric acid and hydrogen peroxide. Determine the lead and cobalt by any convenient method.

Time of Drying on Glass.—Flow the oil over a perfectly clean glass plate and allow to drain in a vertical position in a well-ventilated room at a temperature between 15° and 39° C. After about 2 hours the film is tested at intervals with the finger at points not less than 2½ cm. from the edges. The film will be considered dry when it adheres no longer to the finger and does not rub up appreciably when the finger is rubbed lightly across the surface. With boiled linseed oil this usually occurs in from 5 to 18 hours.

Reagents for Testing.—The following reagents will be required:

Acetone that will pass the specification of the United States Pharmacopoeia.

Acid Calcium Chloride Solution.—Saturate with calcium chloride a mixture of 90 parts water and 10 parts concentrated hydrochloric acid (specific gravity 1.2).

Standard Sodium Thiosulfate Solution.—Dissolve pure sodium thiosulfate in distilled water that has been well boiled to free it from carbon dioxide in the proportion so that 24.83 grams crystallized sodium thiosulfate will be present in 1000 ml. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

Starch Solution.—Stir up 2 to 3 grams of potato starch or 5 grams soluble starch with 100 ml. of 1% salicylic acid solution, add 300 to 400 ml. boiling water, and boil the mixture until the starch is practically dissolved. Dilute to 1 liter.

Potassium Iodide Solution.—Dissolve 150 grams of potassium iodide free from iodate in distilled water and dilute to 1000 ml.

Wijs Solution.—The preparation of the iodine monochloride solution presents no great difficulty, but it should be done with care and accuracy in order to obtain satisfactory results. There shall be in the solution no sensible excess either of iodine or more particularly of chlorine over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary. Dissolve iodine in glacial acetic acid that has a melting point of 14.7° to 15° C. and is free from reducing impurities in the proportion so that 13 g. of iodine will be present in 1000 ml. of solution. Set aside a small portion of this solution while pure and pass dry chlorine into the remainder until the halogen content of the solution is doubled. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged, there will be a slight excess of chlorine which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

Standard Sodium Hydroxide Solution.—Prepare a stock concentrated solution of sodium hydroxide by dissolving sodium hydroxide in water in the pro-

portion of 200 grams NaOH to 200 ml. water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 ml. and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid (C_6H_5COOH) using phenolphthalein as indicator. This solution will be approximately one-fourth normal, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it.

Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95% ethyl alcohol in the proportion of about 22 grams per 1000 ml. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g. to 1000 ml.), kept at about 50° C. for 15 days, and then distilled.

Half Normal Sulfuric Acid Solution.—Add about 15 ml. sulfuric acid (1.84 specific gravity) to distilled water, cool and dilute to 1000 ml. Determine the exact strength by titrating against freshly standardized sodium hydroxide or by any other accurate method. Either adjust to exactly half normal strength or leave as originally made, applying appropriate correction.

Examination of Tung Oil (Chinese Wood Oil)

So far as they apply the methods given above for the analysis of linseed oil and similar oils may be used for the examination of tung oil. The heating test and the quality test given below are special tests for tung oil.

Properties and Tests: Properties (A. S. T. M.).—Raw tung oil shall conform to the following requirements:

	Maximum	Minimum
Specific gravity at $\frac{15.5° \text{ C.}}{15.5°}$	0.943	0.940
Acid number (Alcohol-Benzol)	8	—
Saponification number	195	190
Unsaponifiable matter, per cent	0.75	—
Refractive index at 25° C.	1.520	1.5165
Iodine number (Wijs)	—	163
Heating test, minutes (Browne heat test, see below)	12	—

Gelation Tests for Tung Oils.—One of the unique characteristics of tung oil is gelation when subjected to heating. This gelation is the result of polymerization reactions accelerated by heat and probably also by certain catalysts.

Browne Heat Test.—This test has been a part of the A. S. T. M. specifications for tung oil for many years. The apparatus as slightly revised in 1935 is shown in Fig. 265.

The test tubes for the oil shall be 15 cm. by 16 mm., with a mark near the bottom to indicate 5 ml. Each tube shall be closed by a cork so perforated that a glass rod 3 mm. in diameter may be moved freely. The tubes shall

each weigh 14.5±2.0 g. (The purpose of this requirement is to control the wall thickness.)

Fill a 1000-ml. tall-form glass beaker (height 19 cm., diameter about 9 cm.) with cottonseed oil or other suitable oil to a height of 11 cm. Place the thermometer as shown in Fig. 265 so that the bottom will be level with the bottoms of the test tubes.

Use a nitrogen-filled chemical thermometer, engraved stem, total length 4 to 4½ in., graduated from 210° to 310° C. in 2° C. intervals; the length between 210° and 310° C. not less than 2½ in. Thermometer glass shall be well annealed. This thermometer may be suspended in the bath by a wire or may be sealed to a glass rod as shown in Fig. 265.

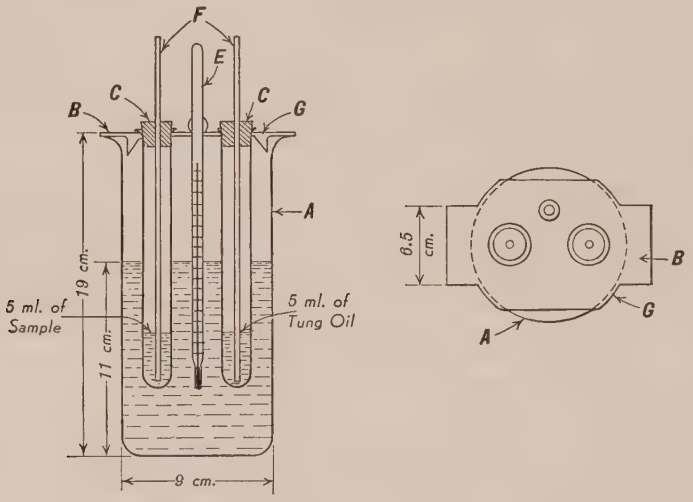

Fig. 265.—Apparatus for Browne Heat Test.

A. 1000-ml. tall-form beaker, 9 cm. in diameter by 19 cm. in height.
B. Support plate about 6.5 cm. wide, made of Monel metal, aluminum or stainless steel.
C. Corks.
D. Test tubes 15 cm. by 16 mm.
E. Thermometer, range 210 to 310 C.
F. Glass rods 3 mm. in diameter.
G. Guide to prevent cover from slipping.

When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 ml. of the oil to be tested and the tube containing 5 ml. of a control sample of known value into the large holes of the cover. Note the time. Remove the source of heat for about 45 sec. and then re-apply. Before 2 min. have elapsed the temperature of the bath will have fallen to 282.2° C. (540° F.), at which point it should be kept as steady as possible. When the samples have been in the bath 9 min. raise the glass rods at intervals of 15 sec. Note the time when each sample becomes firmly set. At this period the oil will be so stiff that the entire tube may be lifted by aid of the rod. As setting or jellying takes place within a few seconds of fluidity, a good end point is afforded. Remove the samples. Heat the bath again to 293° C. (560° F.), and repeat the experiment with fresh portions of the sample.

No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the bath oil has become tarry and viscid, it should be renewed; otherwise heating may be irregular.

High quality tung oil should gel in not over 12 minutes by this test. Raw oiticica oil requires about 18 to 22 minutes.

Worstall Heat Test.—This test consists in heating a quantity of the oil in an open container. Various refinements have been suggested by investigators, such as the use of a polished nickel dish, automatic temperature control, mechanical stirring, etc. However, the following A. S. T. M. method based on Worstall's test, and slightly revised in 1935, is probably as rigorous as needed.

This test requires (1) an ordinary vitreous enamelled iron casserole having a bottom diameter of 7.5 cm. (3 in.), (2) a wide flange tripod with a 7.5 cm. (3 in.) opening (the object of the flange is to prevent super-heating of the sides of the casserole), (3) a total immersion chemical thermometer, range 30–300° C. and 14–15 inches in length.

Put into the casserole 150 g. of the oil and heat so that the temperature reaches 282.2° C.±1° (540° F.±2°) in 4 minutes, ±30 seconds, stirring with the thermometer. Turn down the flame and hold the heat as near 282.2° C. ±1° (540° F.±2°) as possible, stirring with the thermometer, until on lifting the latter, the oil drops with a pronounced string, showing that polymerization has started. The time required after reaching 282.2° C.±1° (540° F.±2°) until the string is noted, is the time of the heat test. For pure tung oils this will not exceed eight minutes. As soon as the oil strings, remove the lamp

Constants of Various Oils

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index
Raw Linseed Oil	.931	186	188	2.0	1.4867
Soybean Oil	.924	129	189	2.3	1.4813
Menhaden Oil	.932	158	187	3.9	1.4850
Raw Tung Oil	.942	166	183	3.8	1.5200
Perilla Oil	.94	200	188	2.0	1.4874
Heavy Bodied Linseed Oil	.968	133	189	2.8	1.4966
Lithographic Linseed Oil	.97	102	199	2.7	1.4978
Whale Oil	.924	148	191	9.2	1.4820
Boiled Linseed Oil (Linoleate Drier)	.941	172	187	2.7	1.4895
Boiled Linseed Oil (Resinate Drier)	.936	184.2	187.6	7.3	1.4895
Corn Oil	.921	124.8	190.1	4.1	1.4800
Cottonseed Oil	.920	111.7	194.3	0.9	1.4781
Rosin Oil	.964	68.9	35.5	32.4	—
Lumbang Oil	.927	152	189	1.0	1.4789
Sunflower Oil	.924	124.6	189.3	7.5	1.4796
Hempseed Oil	.927	149.4	191.1	3.9	1.4822
Shark Oil	.910	132.8	158.9	5.2	1.4815
Sardine Oil	.919	134.6	177.3	10.4	1.4800
Petroleum Mixing Oil	.851	28.2	52.9	1.1	1.4773
Peanut Oil	.932	102.2	188.0	2.2	1.4790
Oiticica Oil	.969	148	189	6.0	1.5141

and the thermometer, and stir with a stiff spatula until the oil is solid. After stringing, a pure tung oil will require not over 40 seconds more to become solid. When solid, allow to stand just one minute, then turn out, upside down, on clean paper and cut at once with a clean spatula. Pure tung oil gives a gel that is dry, not adhering to the spatula when cut, that is firm, crumbling under pressure of the spatula without sticking, and the cut portions should crumble under pressure like dry bread crumbs. Adulterated tung oil gives a gel that is soft, sticky, and which will not crumble.

Examination of Turpentine

Recommended Methods of the A. S. T. M.

Turpentine appears on the market under four types, gum spirits of turpentine, steam-distilled wood, sulfate wood and destructively-distilled wood turpentine. The physical requirements for the first three types are identical except for odor. The requirements of the A. S. T. M. specifications for these types are:

	Gum Spirits, Steam-distilled Wood, Sulfate Wood		Destructively Distilled Wood	
	Maximum	Minimum	Maximum	Minimum
Specific gravity, 15.5/15.5° C.	0.875	0.860	0.875	0.860
Refractive index (n*D*) at 20° C.	1.478	1.465	1.483	1.463
Residue after polymerization with 38 N H_2SO_4:				
Volume (per cent)	2.0	—	2	—
Refractive index (n*D*) at 20° C.	—	1.500	—	1.480
(This residue shall be viscous and its color straw or darker.)				
Initial boiling point at 760 mm. pressure	160° C.	150° C.	157° C.	150° C.
Distilling below 170° C. at 760 mm. pressure (per cent)	—	90	—	90

Color.—Fill a 200-mm., perfectly flat-bottom colorimetric tube graduated in millimeters to a depth of from 40 to 50 mm. with the turpentine to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter, place a No. 1 yellow Lovibond glass and run in the same turpentine until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the turpentine in the two tubes. If this difference is 50 mm. or more the turpentine is " Standard " or better.

Or, compare the color of the sample in any suitable apparatus with the color of an equal depth of a fresh solution of potassium bichromate in distilled water containing 0.0180 g. of potassium bichromate per liter. If the sample is as light as, or lighter than, the bichromate solution, the turpentine is " Standard " or better.

Specific Gravity.—Determine specific gravity at 15.5/15.5° C. by any convenient method that is accurate within 2 points in the fourth figure.

Refractive Index.—Determine refractive index at any convenient temperature with an accurate instrument, and calculate the results to 15.5° C., using the factor 0.00045 for each degree that the temperature of determination differs from 15.5° C.

Distillation.—The distillation range of turpentine is obtained with special apparatus and technique which are described in the A. S. T. M. and the Federal specifications. In order to obtain results comparable with those of other analysts, the details of the test must be followed closely. The instructions are too long to include in a book of this character and it is therefore recommended that analysts making this test obtain copies from one of the sources given above.

Polymerization.—Place 20 ml. of exactly 38/N (100.92%) sulfuric acid [3] in a graduated, narrow-neck Babcock flask, stopper, and cool in ice-water. Add slowly 5 ml. of the turpentine to be tested. Gradually mix the contents, cooling from time to time, and do not allow the temperature to rise above about 60° C. When the mixture no longer warms up on shaking, agitate thoroughly and place the bottle in a water bath and heat at 60 to 65° C. for about ten minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking five or six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to room temperature, fill the flask with concentrated sulfuric acid until the unpolymerized oil rises into the graduated neck. Centrifuge at about 1200 R.P.M. from four to five minutes, or allow to stand for twelve hours. Calculate the amount of unpolymerized residue, notice its consistency and color, and determine its refractive index.

ANALYSIS OF VARNISH

The testing of varnish should be largely of a physical nature. Such properties as odor, consistency, clarity, flowing, time of drying, character of finish, hardness, resistance to moisture and abrasion, elasticity, etc., point out the real value of a varnish. Other tests that give additional information, sometimes of a valuable nature, are as follows: Flash point, acid number, ash, character of solvent, fixed oil and resins.

Flash Point.—A nickel or iron crucible of 60 mm. diameter and 40 mm. height is filled with the varnish to within 20 mm. of the top. It is then supported in a water bath in such a manner as to be about two-thirds immersed in the water. The water should be from 15° to 20° C. at the start and should be heated slowly so that the temperature of the varnish, as indicated by a

[3] Made by mixing fuming sulfuric acid with concentrated sulfuric acid. For details see specification of the A. S. T. M. or of the Federal Specification Board.

thermometer suspended in it, will show a rise of about 1 degree per minute. Test for flash at each half degree, using a very small flame.

Acid Number.—Ten to 20 grams of the varnish are weighed into a small Erlenmeyer flask, 50 ml. neutral alcohol added, and a small funnel inserted in the neck. Heat on the water bath for one-half hour, with occasional shaking. Allow to cool somewhat, add two drops of phenolphthalein indicator and titrate with tenth-normal potassium hydroxide solution. The acid number is the number of milligrams of KOH required to neutralize each gram of the varnish.

Ash.—Weigh in a porcelain or fused silica crucible several grams of the varnish. Burn off over a small Bunsen flame, using great caution to avoid boiling over and spattering. When all combustible matter is destroyed, weigh the ash and if desired analyze it.

Solvent.—Steam distillation of a portion of the varnish will remove the solvents, leaving a residue of fixed oils and varnish resins, which may be weighed after driving off the water. The distillate should be examined as recommended under Methods for the Examination of Turpentine. The amount of mineral spirits and turpentine may thus be determined.

Fixed Oils and Resins.—In the above determination, the total amount of fixed oils and resins is obtained. It is a difficult matter, however, to determine the exact percentage and character of resins that have been used in the manufacture of the varnish. This is due to the fact that during the process of heating oils in the presence of resins many intricate chemical changes are brought about, a considerable portion of the resins being distilled off in the form of vapors and combinations of the oil brought about that are difficult of separation. One of the best methods, however, of separating the fixed oils and varnish resins is carried out in the following manner.

About a half ounce of the varnish resin should be placed in a 300-ml. tared beaker. There should then be added about 200 ml. of ice-cold petroleum ether and the beaker should be covered and allowed to stand, preferably in a dish containing ice. In an hour's time the resinous ingredients will be found precipitated at the bottom of the beaker or adhering to the side thereof (with the exception of rosin, which is largely soluble in petroleum ether). The precipitated resins should be washed with fresh portions of cold petroleum ether two or three times, pouring the decanted portions into a large bottle. The combined portions of petroleum ether may then be filtered through a tared filter, adding by the aid of a stirring rod the resins contained in the beaker. The filter paper and the beaker with the resins may then be dried at 100° C. and weighed. The combined filtrates may be distilled to obtain the fixed oil which may be examined for constants. (This fixed oil may contain rosin.) The amount of rosin contained in a varnish may be roughly ascertained by thoroughly shaking in a separatory funnel a portion of the varnish with a large quantity of absolute alcohol. The rosin may be obtained by evaporation of the alcoholic extracts. The fixed oils after oxidation or polymerization, as caused by the heating of the varnish during manufacture, are not readily soluble in alcohol.

Separation of Polymerized Oils and Resins.—In the making of varnish, some oils become oxidized or polymerized to a condition resembling resins. For instance, when a varnish is examined for resins by the above method, it will often be found that a considerable amount of matter insoluble in petroleum

ether will be obtained even when hard resins are absent. The insoluble substance is oxidized or polymerized oil. It may be differentiated from varnish resins by the fact that it is readily saponified by alcoholic potash. The following method by Boughton (Technologic Paper No. 65, U. S. Bureau of Standards), though involving considerable work, is probably the most accurate method for the separation of polymerized oils and resins.

To about 4 grams of varnish in a flask add about 25 ml. of water and boil until the volume is about 10 ml. This removes nearly all of the volatile. Add 25 ml. half normal alcoholic potash and 25 ml. benzol and boil under a reflux condenser for one-half hour. Evaporate the solution to about 15 ml. and add about 10 ml. of alcohol. Transfer completely to a separatory funnel, washing the flask with water and ether and using a policeman if necessary. Dilute with water to about 100 ml., add 100 ml. of ether, and shake. Add a few ml. of alcohol if necessary to make the layers separate. Draw off the aqueous layer and wash the ether three times with water and transfer to a tared flask for future use.

To the combined soap solution and washings, add an excess of hydrochloric acid and extract twice with 50 ml. of ether. Discard the aqueous layer, wash the combined ether extracts with water, transfer to a flask and distill off the ether. To the dry residue add 20 ml. of absolute alcohol and 20 ml. of a mixture of 1 volume of sulfuric acid and 4 volumes of absolute alcohol and boil for two minutes under a reflux condenser. Completely transfer the contents of the flask to a separatory funnel, washing the flask with water and ether. Add 100 ml. ether and after agitation add 100 ml. of 10 per cent sodium chloride solution and again shake. Draw off the aqueous layer, extract it with 50 ml. of ether, combine the ether solutions and wash with water. Add 50 ml. of a fifth-normal potassium hydroxide solution and 10 ml. of alcohol, shake and draw off the lower layer into a second funnel. Wash the ether layer with 50 ml. of water containing 5 ml. of the potassium hydroxide solution and 5 ml. of alcohol.

Extract the combined aqueous portions with two 50 ml. portions of ether and finally wash the combined ether solutions (containing the ethyl esters of the fatty acids) with water.

Distill off the ether and boil the residue with 25 ml. of half-normal alcoholic potash for one-half hour under a reflux condenser. Transfer completely to a separatory funnel and extract the soap four times with ether. Wash the combined ether solution twice with water and add it to the first ether solution of unsaponifiable matter obtained.

Unite the solution and washings containing the soaps, add an excess of hydrochloric acid, and extract twice with ether. Transfer to a tared flask the combined ether solutions, after washing them with water, distill off the ether, dry the residue to constant weight at 110° C. and weigh as "fatty acids."

Report the percentage of fatty acids as percentage of oil and calculate the percentage of resin by difference.

OTHER MATERIALS

For detailed methods other than those given in this book for the examination of shellac, resins, bitumens, and other like materials for the vehicle portion of paints and varnishes, the following references may be consulted:

A. S. T. M. Standards on Preservative Coatings for Structural Materials. American Society for Testing Materials, Philadelphia, Pa.
Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors, 9th Edition, by Henry A. Gardner. Henry A. Gardner Laboratory, Inc., 2201 New York Avenue, N.W., Washington, D. C.
Federal Specifications of the Procurement Division of the U. S. Treasury Department. Superintendent of Documents, Government Printing Office, Washington, D. C.

THE ANALYSIS OF PAINT PIGMENTS

The liquid having been extracted from the paint under examination, by the previously outlined methods, the pigment is left ready for analysis. The pigment can readily be classified under one of the following heads by its color, thus shortening any preliminary examination. Many of the colors have a white base which necessitates a determination of both the colored portion of the pigment and any white base which may have been used.

The general analysis of colored pigments is carried out according to the specific method outlined for the individual colored pigments, together with the methods for a composite white paint, provided a qualitative examination does not directly reveal the identity of the pigment.

The pigments used in the manufacture of paints are classified as follows, in certain instances the trade names being given by which the particular pigments are known.

White Pigments

Lead Pigments

Basic Sulfate of Lead—Basic Sulfate White Lead.
Basic Carbonate of Lead—Old Dutch Process White Lead—Quick Process White Lead—Mild Process White Lead.
Zinc Lead—Leaded Zinc.

Zinc Pigments

Zinc Oxide—Zinc White.
Lithopone.
Titanated Lithopone.

Other Opaque White Pigments

Titanium Oxide.
Titanium-Barium Pigment.
Titanium-Calcium Pigment.
Antimony Oxide.
Lead Titanate.
Zirconium Oxide.

Silica Pigments

Silica—Silex.
Asbestine—Talcose.
China Clay—Kaolin.

Calcium Pigments

Whiting—Paris White—Chalk—Alba Whiting—Spanish White.
Gypsum—Plaster of Paris—Terra Alba—Agalite.

Barium Pigments

Barytes—Barite—Blanc Fixe—Barium Sulfate.
Barium Carbonate—Witherite.

Red and Brown Pigments

Red Lead—Orange Mineral.
Vermilion.
Ochres—Tuscan Red—Indian Red—Venetian Red.
Umbers—Siennas.

Blue Pigments

Sublimed Blue Lead.
Ultramarine Blue—Phthalocyanine Blue.
Prussian Blue—Antwerp Blue—Chinese Blue.

Yellow and Orange Pigments

Chrome Yellow—Lemon Chrome Yellow—Medium Chrome Yellow.
American Vermilion Orange Chrome—Basic Lead Chromate.
Orange Mineral.
Hansa Yellow.

Green Pigments

Chrome Green (mixture of Lead Chromate and Prussian Blue).
Chromium Oxide.
Green Earth.

Black Pigments

Graphite.
Carbon Black—Bone Black—Lamp Black—Drop Black—Ivory Black.
Willow Charcoal.
Black Oxide of Iron.

ANALYSIS OF WHITE PIGMENTS

Basic Sulfate of Lead

Basic Sulfate White Lead. Sublimed White Lead. Super Sublimed White Lead

This pigment, embracing the daily analysis by the manufacturers of the product of over five months' time, shows the following average composition:

Lead sulfate	76.68%
Lead oxide	17.23
Zinc oxide	5.79
	99.70

The remaining .3 of 1% consists of moisture and ash which are rarely determined.

The analysis of this pigment based on the following method,[4] which depends upon the above average composition, together with the volumetric determination of the total lead and zinc contents, is rapid and accurate.

Volumetric Determination of Lead[5]

One gram of the sample is dissolved in 100 ml. of an acid ammonium acetate solution made up as follows:

Eighty per cent acetic acid	125 ml.
Concentrated ammonium hydroxide	95 ml.
Water	100 ml.

Add this solution hot, dilute with 50 ml. water and boil until a clear solution is obtained. Dilute to 200 ml. and titrate with standard ammonium molybdate solution, using a freshly prepared solution of tannic acid as an outside indicator.

A solution of ammonium molybdate containing 8.67 grams per liter usually gives a solution where,

$$\text{One ml.} = 0.01 \text{ gram Pb.}$$

Standardize against pure PbO, pure $PbSO_4$, or clean lead foil.

For further details of this method see p. 511.

The gravimetric method given under Basic Carbonate of Lead may be preferred.

Volumetric Determination of Zinc

Dissolve 1 gram of the pigment in concentrated hydrochloric acid, adjust the acidity to 3 ml. of concentrated hydrochloric acid, dilute to 200, heat to above 60° C., and titrate with standard potassium ferrocyanide solution, using a fresh 5% uranium nitrate solution as an outside indicator. Calculate the zinc to zinc oxide.

[4] Ind. Eng. Chem., **6**, 200 (1914).

[5] Modification of Low's Method, "Technical Methods of Ore Analysis," p. 149.

Calculation of Composition

Using the average total of 99.70%, the total lead found and the zinc oxide content, the composition of this pigment is determined by the following calculation:

Total percentage of lead compounds present
= total percentage found of ZnO, PbO and $PbSO_4$ − percentage of ZnO.
Total percentage of lead compounds present
= 99.70% (average total) − percentage ZnO.

Atomic weight lead	207.2
Molecular weight lead oxide	223.2
Molecular weight lead sulfate	303.2

As a hypothetical case, we can assume the presence of a 4.70% ZnO and 69.00% metallic lead.

$$\frac{\left(\frac{\text{Mol. wt. } PbSO_4}{\text{At. wt. Pb}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\frac{\text{Mol. wt. } PbSO_4 - \text{mol. wt. PbO}}{\text{Mol. wt. PbO}}} = \%\ \text{PbO present}$$

$$\frac{\left(\frac{\text{Mol. wt. PbO}}{\text{At. wt. Pb}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\frac{\text{Mol. wt. PbO} - \text{Mol. wt. } PbSO_4}{\text{Mol. wt. } PbSO_4}} = \%\ PbSO_4\ \text{present.}$$

Determining the percentage of lead oxide and lead sulfate present by the above formulas we find:

$$\frac{\left(\frac{303.1}{207.1} \times 69.00\right) - 95.00}{\frac{303.1 - 223.1}{223.1}} = \text{per cent PbO} = 16.68$$

$$\frac{\left(\frac{223.1}{207.1} \times 69.00\right) - 95.00}{\frac{223.1 - 303.1}{303.1}} = \text{per cent } PbSO_4 = 78.32.$$

If it is necessary actually to determine the percentage of lead sulfate present, the following procedure may be followed:

Total Lead Sulfate

Mix 0.5 gram of the sample with 3 grams of sodium carbonate. Add 30 ml. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute with hot water, filter and wash thoroughly. All the lead sulfate is here

changed to lead carbonate, the sodium carbonate being transposed to sodium sulfate, which is found in the filtrate.

The sulfate is determined in the filtrate by precipitation as $BaSO_4$. Calculate the $BaSO_4$ to $PbSO_4$. Determine the total lead as above outlined, deduct the lead found as $PbSO_4$ and calculate the residual lead to PbO.

The foregoing method is the one generally used in the commercial estimation of lead and yields excellent results to the analyst who is familiar with it. However, in laboratories where only occasional lead determinations are made, the well-known gravimetric methods for lead and zinc will sometimes be found preferable. The time required for gravimetric determinations is not much greater and the chance of error is reduced.

The method referred to consists in weighing the lead as chromate [6] and the precipitation of the zinc from the filtrate with sodium carbonate, igniting it, and weighing as zinc oxide.

Super Sublimed White Lead

Super Sublimed White Lead is an extremely white basic sulfate of lead pigment. Chemically, it contains no zinc oxide, being a true basic sulfate of lead showing approximately 25% lead oxide, the balance being lead sulfate. Its physical properties are similar to sublimed white lead, its distinguishing characteristics being its extreme whiteness.

The analysis of this pigment is an exceedingly simple procedure. If it is desired to determine the sulfate present, the method as outlined under sublimed white lead can be used. All the sulfate is calculated as lead sulfate after determination of total lead and sulfate, the difference between the lead present as lead sulfate and the total lead present being calculated as lead oxide.

The analysis of this pigment can be further simplified by a simple determination of the total lead present and the calculation followed for the determination of the lead sulfate and lead oxide as outlined under sublimed white lead. In this latter calculation, however, it must be remembered that the total sum of the lead constituents present represents 100%, instead of the difference between 99.70% and the percentage of zinc oxide present in sublimed white lead. This is due to the fact that super sublimed white lead shows the presence of no zinc oxide or insoluble residue. By the simple substitution of 100.00 in place of the determined per cent Pb constituents in the formula and the determination of the total lead present, the analysis can be completed in a rapid way.

[6] As outlined under Basic Carbonate of Lead.

BASIC CARBONATE OF LEAD

Basic Carbonate White Lead.[7] Old Dutch Process White Lead. Quick Process White Lead

Basic carbonate white lead contains approximately 80% metallic lead and 20% carbonic acid and combined water with traces sometimes of silver, antimony and other metals. The formula for this compound is $2PbCO_3 \cdot Pb(OH)_2$.

Total Lead (Gravimetric)

Dissolve 1 gram in 20 ml. of HNO_3 (1 : 1) in a covered beaker, heating till all CO_2 is expelled; wash off cover, add 20 ml. of H_2SO_4 (1 : 1) and evaporate to fumes of SO_3, cool, add about 150 ml. of water and 150 ml. of ethyl alcohol; let stand in cold water one hour, filter on a Gooch crucible, wash with 95% ethyl alcohol, dry at 110° C., and weigh the $PbSO_4$. Calculate to PbO or to basic carbonate.[8] Instead of determining the lead as sulfate, the sample may be dissolved by boiling with acetic acid; then dilute to about 200 ml. with water, make alkaline with NH_4OH, then acid with acetic acid, heat to boiling and add 10 to 15 ml. of a 10% solution of potassium dichromate; heat till the yellow precipitate assumes an orange color. Let settle and filter on a Gooch crucible, washing by decantation with hot water till the washings are colorless, finally transferring all of the precipitate. Then wash with 95% ethyl alcohol and then ether; dry at 110° C. and weigh $PbCrO_4$. (Any insoluble matter should be filtered out before precipitating the lead.)

Total Lead (Volumetric)

Dissolve 0.5 gram of sample in 10 ml. of concentrated hydrochloric acid, boil till solution is effected, cool, dilute to 40 ml. and neutralize with ammonium hydroxide. Add acetic acid until distinctly acid, dilute to 200 ml. with hot water, boil and titrate with ammonium molybdate as follows:

Dissolve 4.25 gram of ammonium molybdate in water and make up to one liter. To standardize this solution, dissolve about 0.2 gram of pure lead foil in nitric acid (pure PbO or $PbSO_4$ may also be used), evaporate nearly to dryness, add 30 ml. of water, then 5 ml. H_2SO_4 (sp.gr. 1.84), cool, and filter.

Drop filter with $PbSO_4$ into a flask, add 10 ml. concentrated HCl, boil till completely disintegrated, add 15 ml. of HCl, 25 ml. of water, and NH_4OH till alkaline. Acidify with acetic acid, dilute to 200 ml. with hot water and boil. Titrate, using an outside indicator of one part of tannic acid in 300 parts of water.

It should be noted that when calcium is present, it forms a more or less insoluble molybdate, and results are apt to be high. With samples containing less than 10% of lead, the lead should be precipitated as $PbSO_4$, filtered, redissolved and titrated as in the process of standardizing.

[7] Routine Analysis of White Pigments. American Society for Testing Materials.

[8] This method of weighing lead sulfate is not accurate in the presence of calcium compounds.

Carbon Dioxide

Determine by evolution with dilute hydrochloric acid, absorbing the carbon dioxide in soda-lime or KOH solution. Calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

Acetic Acid [9]

Place 18 grams of the pigment in a 500-ml. flask, add 40 ml. of sirupy phosphoric acid, 18 grams of zinc dust and 50 ml. of water. Connect to a straight Liebig condenser, apply heat and distill down to a small bulk. Then pass steam into the flask until it becomes about half full of condensed water, shut off the steam and distill down to a small bulk—this operation being conducted twice. To the total distillate which was collected in a larger flask add 1 ml. of sirupy phosphoric acid, connect to a Liebig condenser, using a spray trap, and distill to a small volume—about 20 ml. Pass steam through till about 200 ml. of water condenses in the distillation flask, shut off steam and continue the distillation. These operations of direct and steam distillations are conducted until 10 ml. of the distillate require only 1 drop of 0.1 N alkali to give a change in the presence of phenolphthalein. Then titrate the total distillate with 0.1 N sodium hydroxide and phenolphthalein and calculate the total acidity as acetic acid. It will be found convenient to titrate each 200-ml. portion of the distillate as collected.

Metallic Lead

Weigh 50 grams of the sample into a 400-ml. beaker, add a little water and add slowly 60 ml. of 40% acetic acid and after effervescence has ceased, boil on hot plate. Fill the beaker with water, let settle, and decant the clear solution. To the residue add 100 ml. of a mixture of 360 ml. of conc. NH_4OH, 1080 ml. of water, 2160 ml. of 80% acetic acid, and boil until all solution is complete. Fill the beaker with water, let settle and decant the clear solution. Collect residue on a watch-glass, floating off everything but metallic lead. Dry and weigh. Result $\times 2$ = percentage of metallic lead in sample.

The following method of A. N. Finn (unpublished) gives total basicity of a pure white lead: Place 2 grams of pigment in an evolution flask, add a little CO_2-free water, connect with a separatory funnel and condenser (Knorr type), add through the funnel, finally washing down, 100 ml. of N/4 nitric acid, boil and absorb the CO_2 in a soda lime tube in the usual manner (having H_2SO_4 and $CaCl_2$ drying tubes in train) and weigh. To the solution in the evolution flask, add about 20 ml. of neutral sodium sulfate solution and titrate with N/4 sodium hydroxide solution (carbonate-free), using phenolphthalein. CO_2 is calculated to $PbCO_3$. The amount of N/4 acid corresponding to the CO_2 is calculated and deducted from the total amount of N/4 acid neutralized by the sample and the difference calculated to combined H_2O, from which $Pb(OH)_2$ is computed.

[9] Thompson's Method, Jour. Soc. Chem. Ind., 24, 487 (1905).

ZINC LEAD AND LEADED ZINC

Zinc lead and leaded zinc are varying compounds containing zinc oxide and lead sulfate, the former showing approximately 50% zinc oxide and 50% lead sulfate, while the latter contains on an average 25% lead sulfate and 75% zinc oxide. The most widely used type is probably that with 35% basic lead sulfate. See also pp. 509, 1060, Vol. I.

These pigments may be analyzed by the following procedure:

Moisture.—Heat 2 grams at 105° C. for two hours. Cool and weigh.

Lead and Zinc.—Determine the lead directly by the method given under Basic Carbonate of Lead, and the zinc by the volumetric ferrocyanide method as outlined under Sublimed White Lead. See also pages 509 and 1060, Vol. I.

Total Soluble Sulfates [10] (in the absence of $BaSO_4$).—Treat 0.5 gram of the sample with 5 ml. of water, 3 grams of NH_4Cl and 5 ml. of HCl saturated with bromine; digest (covered) on the steam bath about fifteen minutes, add 25 ml. of H_2O, neutralize with dry Na_2CO_3 and add about 2 grams more. Boil ten to fifteen minutes; let settle, dilute with hot water, filter and wash with hot water; redissolve in HCl, reprecipitate as above and wash thoroughly with hot water. Acidify the united filtrates with HCl and add a slight excess of 10% $BaCl_2$ solution. Let stand on steam bath for one hour, filter, wash with hot water, ignite and weigh the $BaSO_4$. Calculate to SO_3 (includes SO_3 formed from SO_2).

Total Soluble Sulfate (in the presence of $BaSO_4$).—Treat 1 gram in a 600-ml. beaker with 10 ml. of H_2O, 10 ml. of strong HCl, saturated with bromine, and 5 grams of NH_4Cl, heat on a steam bath in a covered beaker for five minutes, add hot water to make about 400 ml., boil for five minutes and filter to separate any insoluble material. (A pure pigment should be completely dissolved.) Wash with hot water, ignite and weigh the insoluble. Remove lead with Na_2CO_3 as above, making a double precipitation, acidify, and to the boiling hot filtrate add slowly, with stirring, 20 ml. of a 10% $BaCl_2$ solution; let stand for two hours on the steam bath, filter, wash, ignite, and weigh as $BaSO_4$. (Includes SO_3 formed from SO_2.)

Soluble Zinc Sulfate.—Heat nearly to boiling 2 grams of the sample with 150 ml. of water and 50 ml. of alcohol for thirty minutes, filter and wash with a mixture of alcohol and water (1 : 3). Heat the filtrate to boiling and expel most of the alcohol; then determine SO_3 by the usual method of precipitation with $BaCl_2$. Calculate to $ZnSO_4$ and to SO_3.

Sulfur Dioxide.—Digest 2 grams of the sample with frequent stirring in 100 ml. of freshly boiled cold water and 5 ml. of concentrated HCl; let stand ten to fifteen minutes, add an excess of 0.01 normal iodine solution and titrate back with 0.01 normal sodium thiosulfate solution, using starch indicator. Report as SO_2. Run blank on reagents and make corrections.

Calculations.—Report soluble SO_3 as $ZnSO_4$. Deduct ZnO equivalent of the $ZnSO_4$ from total ZnO and report residue as ZnO. Deduct soluble SO_3

[10] Report of Sub-committee VIII of Committee D-1, Proceedings of American Society for Testing Materials, **14**, 271–2, 1914.

and SO_3 equivalent to SO_2 from total SO_3, calculate remainder to $PbSO_4$; subtract PbO equivalent of $PbSO_4$ from total PbO and report remainder as PbO.

ZINC OXIDE

Moisture.—Heat 10 grams on watch-glass for two hours at 105 to 110° C. Cool and weigh.

Zinc Oxide.—Using a 0.25 g. sample, determine zinc as outlined under Basic Sulfate of Lead.

Total Soluble Sulfur.—Moisten 10 g. of the pigment with alcohol, add a few drops of Br_2, or about 5 ml. of Br-water, then concentrated HCl in excess; boil to expel the Br_2; filter off any insoluble matter, and wash the paper with hot water.

Nearly neutralize the clear solution in a covered beaker with NaOH solution, complete the neutralization with dry Na_2CO_3 and add about 2 g. more of this reagent. Boil 10 to 15 minutes, wash off cover, let settle, filter, and wash with hot water. Redissolve the precipitate in HCl (1 : 1), reprecipitate with Na_2CO_3 as above, filter, and wash thoroughly with hot water. Acidify the united filtrates with HCl, adding about 1 ml. in excess. Boil to expel bromine and to the clear boiling solution add slowly with stirring an excess of a 10% $BaCl_2$ solution. Let stand on a steam bath for at least 1 hour, filter on a weighed Gooch crucible, wash thoroughly with boiling water, dry, ignite at a dull red heat, cool, and weigh as $BaSO_4$. This will include soluble sulfates, SO_3 formed from SO_2 and the SO_3 that is formed from sulfide sulfur.

Sulfur Dioxide (Rigg Method).—Make a suspension of 5 g. of the sample in 50 ml. warm water (freshly boiled and then partly cooled), pour into a glass stoppered iodine determination bottle containing 18 ml. of HCl and exactly 25 ml. of 0.1 N iodine solution, and shake until all the oxide is dissolved. Titrate the excess of I_2 as rapidly as possible with 0.1 N thiosulfate solution. If the thiosulfate solution is not exactly 0.1 N, a blank should be run.

Zinc Sulfate.—Proceed as under Zinc Lead and Leaded Zinc.

LITHOPONE

Lithopone, in the restricted sense, is a mixture of equimolar quantities of zinc sulfide and barium sulfate. The commercial pigment contains approximately 28% of the former ingredient and 72% of the latter. Lithopone is produced in several modifications, the principal ones being those in which the extending portion is calcium sulfate or magnesium silicate. High strength lithopone contains from 45 to 60% of zinc sulfide.

Moisture.—Heat 2 grams for two hours at 105° C.

Barium Sulfate.—Treat 1 gram with 10 ml. conc. HCl and 1 gram of potassium chlorate, added in small amounts. Evaporate to one-half its volume, add 100 ml. hot water and a few ml. of dilute H_2SO_4. Boil, filter, wash and weigh the insoluble residue, which should show only the presence of barium sulfate. Examine the residue for silica and alumina.

Zinc Sulfide.—Determine the zinc in the pigment by the method given under Sublimed White Lead. Calculate to zinc sulfide. From this value subtract the zinc sulfide equivalent of the zinc oxide as determined below.

Zinc Oxide.—Digest 1 gram of the pigment with 100 ml. of 3% acetic acid solution for 18 hours. Stir several times during digestion, especially during the first hour. Filter, wash with 3% acetic acid and determine the zinc by the usual method.

Soluble Salts.—Digest 2 grams with hot water and examine the filtrate for soluble salts.

TITANIUM PIGMENTS

The titanium pigments used in paints are: titanium dioxide, barium base pigment, which is a mixture of 25 parts of titanium dioxide and 75 parts of barium sulfate, calcium base pigment, which is a mixture of 30 parts of titanium dioxide and 70 parts of calcium sulfate, titanated lithopone, which is a mixture of 85 parts of lithopone and 15 parts of titanium dioxide, and lead titanate. A mixture of titanium dioxide and magnesium silicate is sometimes found.

Barium Sulfate.—Weigh ½ gram sample into 250-ml. Pyrex glass beaker; add 20 ml. concentrated sulfuric acid and 7 or 8 grams ammonium sulfate. Mix well and heat on hot plate until fumes of sulfuric anhydride are evolved and then heat directly over flame to boiling for five minutes or until solution is complete. Traces of silica, if any, remain as an insoluble residue.

Cool, take up with 100 ml. of water, boil and filter off barium sulfate and silica, washing with 5% sulfuric acid to free residue from titanium. Use the filtrate for the determination of titanium dioxide.

Calcium Sulfate.—Extract the calcium sulfate by boiling 0.5 gram of the pigment in a 250-ml. beaker with 25 ml. of hydrochloric acid (1 : 1) for several minutes. Dilute to 150 ml. with water, boil and filter. Wash the residue with hot hydrochloric acid solution (10 ml. of HCl sp.gr. 1.19 and 990 ml. of water) until the washings show no calcium, when tested with NH_4OH and $(NH_4)_2C_2O_4$. Determine the calcium in the filtrate by the oxalate method.

Titanium Dioxide.—Determine the titanium in the filtrate from the barium sulfate reducing it in a Jones or similar reductor and titrating the reduced solution with a standardized ferric ammonium sulfate or potassium permanganate solution.

Lead Titanate.*—If lead titanate is to be determined, it will be necessary first to separate any other compounds of lead that may be present. If separate determinations of the basic carbonate and basic sulfate of lead are desired, first extract the former with 10% acetic acid solution, and then the latter with 40% neutral ammonium acetate solution; otherwise, extract with acid ammonium acetate solution as directed under Basic Sulfate of Lead. The lead oxide in leaded zinc, if present, will be in the acetic acid extraction. The residue, after extraction, is dried and treated with 25 ml. sulfuric acid and 10 grams ammonium sulfate for each 0.5 grams of residue as directed in the first paragraph under Barium Sulfate. The solution is diluted to 200 ml. and allowed to stand overnight. If barium sulfate is absent, and if no titanium dioxide has been precipitated, the lead sulfate may be filtered, dried and weighed in the usual manner. It is, however, recommended that the precipitate be redissolved in ammonium acetate solution and the lead determined as lead chromate. Calculate the lead as $PbTiO_3$.

This method will account for approximately 92% of the pigment. The remainder is uncombined sulfate, which is not distinguishable from other lead sulfate that may be present.

ANTIMONY OXIDE

Antimony trioxide (Sb_2O_3), a fume pigment that has recently been introduced, may be occasionally found in certain classes of mixed paints. After being brought into solution, it may be quantitatively estimated by oxidation with permanganate or iodine.

ZIRCONIUM PIGMENTS [11]

The usual zirconium pigments, in addition to considerable SiO_2 usually contain less than 0.2% each of TiO_2 and Fe_2O_3. The following simplified method, as modified by Mr. C. J. Kinzie, is based on the procedure of Lundell and Knowles.

Fuse the sample, or the insoluble matter, with Na_2CO_3 in a platinum

* Based on method of D. W. Robertson, Private communication, 1937.

[11] Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors. H. A. Gardner.

crucible, extract the fusion with 30 ml. of H_2SO_4 (1 : 1) and evaporate to strong SO_3 fumes. If considerable residue adheres to the beaker, remove from the heat at the first signs of SO_3 and scrape the residue from walls of the beaker with a glass rod and wash down with H_2SO_4 (1 : 1) from a wash bottle, then continue the heating to strong fumes as directed. Filter and treat the residue with H_2SO_4 and HF. Examine the residue for undecomposed pigment and, if necessary, make a second fusion with Na_2CO_3.

Treat the filtrate from the SiO_2 with NH_4OH and filter. Reject the filtrate and dissolve the precipitate in H_2SO_4 (1 : 1).

Adjust the acidity of the solution to about 1% (by volume) of H_2SO_4 and pass in H_2S to remove the heavy metals. Filter. If desired, analyze the H_2S precipitate by the regular methods.

Adjust the acidity of the filtrate from the H_2S treatment to 10% (by volume) of H_2SO_4, in 400 ml. of solution. Boil to remove H_2S. Cool to between 5° and 14° C.

Add an excess of cold 6% aqueous solution of cupferron to precipitate the zirconium, titanium and iron. An excess of the precipitant is indicated by the formation of a fine white precipitate which redissolves instead of a curdy one, which persists. The color of the cupferron precipitate is an excellent indication of the amount of titanium present, since zirconium precipitates are pure white while the titanium precipitates are yellow. A brownish tint indicates iron or, less likely, vanadium. Filter, after a five-minute digestion, using an ashless filter paper and a platinum cone, with gentle suction. Thoroughly wash the precipitate with cold 10% (by volume) HCl.

Clear filtrate and washings indicate complete precipitation of zirconium and titanium, while cloudy or opalescent ones indicate the reverse. The latter occasionally develops, and no satisfactory explanation has been found. Under these circumstances, recovery must be made as follows: Evaporate the solution to a small volume and destroy the organic matter by digestion with HNO_3, finally heating until fumes of H_2SO_4 appear. Cool, dilute, filter off any SiO_2 resulting from attack on glassware, and repeat the precipitation with cupferron in a 10% H_2SO_4 solution as directed above.

Carefully dry and ignite the paper and precipitate in a tared platinum crucible and finally ignite over a blast lamp or its equivalent. Cool in a desiccator, and weigh as mixed oxides of Zr, Ti, Fe and rare earth. Fuse the mixed oxides with potassium pyrosulfate, take up in 10% (by volume) of H_2SO_4, and determine the iron colorimetrically.

Titanium should be determined on an original sample.

Aluminum is determined in the filtrate from the cupferron treatment. Destroy organic matter by heating with small quantities of HNO_3, finally heating to fumes of SO_3. Dilute, filter off any silica dissolved from the beaker and determine aluminum in the filtrate.

SILICA OR SILEX—CHINA CLAY—ASBESTINE

These pigments, while all true silica pigments, are widely different in physical structure. A microscopic examination is of great value.

The particles of quartz or silex are sharp and irregular, those of china clay are flat, and those of asbestine are rodlike. Diatomaceous earth may sometimes be recognized in siliceous pigments. The color, fineness, and other such properties are more important than chemical analysis. However, if desired, determinations of silica alumina, magnesia, etc., may be made by recognized methods.

Moisture.—Heat 2 grams at 105° for two hours.

WHITING (PARIS WHITE), GYPSUM (PLASTER OF PARIS)

These pigments are of the following composition:

Whiting.—The natural form of calcium carbonate.

Paris White.—The artificial form of calcium carbonate.

Gypsum.—The hydrated form of calcium sulfate, of formula $CaSO_4 \cdot 2H_2O$.

These pigments are analyzed in the following manner:

Moisture.—Heat 2 grams at 105° C. for two hours.

Loss on Ignition.—Ignite 1 gram at a high heat to constant weight. The loss will be water, if carbonates are absent.

Calcium.—Treat 1 gram with dilute HCl and a few drops of HNO_3. Evaporate to dryness, dehydrate, moisten with a few drops of concentrated HCl, dilute with hot water and determine the insoluble residue. Examine for $BaSO_4$. The residue should consist of silica.

In the filtrate, precipitate and determine the iron hydroxide and aluminum hydroxide in the usual manner. The calcium is precipitated in the boiling ammoniacal filtrate with 30 ml. of saturated ammonium oxalate solution, allowing the solution to boil for one-half hour. A double precipitation is here advisable to remove the last traces of magnesium. The calcium oxalate is filtered off, thoroughly washed and determined volumetrically by the permanganate method, p. 211.

Magnesium.—Determine in the filtrates after removal of the calcium by precipitation as magnesium ammonium phosphate and ignition to magnesium pyrophosphate in the usual manner.

Carbon Dioxide.—Determine by the evolution method.

Sulfates.—Dissolve 1 gram in concentrated HCl, remove any insoluble residue, heat to boiling and precipitate any sulfate as $BaSO_4$, determining in the usual manner.

BARYTES AND BLANC FIXE

Of these two barium pigments used in the manufacture of paints, barytes is the natural barium sulfate, while blanc fixe is precipitated barium sulfate. Their barium sulfate content should be not less than 95%.

The following method may be used for the analysis of these pigments:

Moisture.—Heat 2 grams at 105° C. for two hours.

Loss on Ignition.—Ignite 1 gram to constant weight. The loss will be reported as loss on ignition, and will consist of free and uncombined water, carbon dioxide and organic matter.

Barium Sulfate.—Boil 1 gram with dilute HCl, evaporate to dryness, moisten with HCl, add water, boil, filter and wash. Should lead be present in the insoluble residue, as shown by the action of H_2S, treat the insoluble residue with a little (1 : 1) HCl and several drops of H_2SO_4. Filter, wash and weigh the residue. Treat the ignited residue with H_2SO_4 and HF, evaporate to dryness and ignite. The residue should show no loss as silica. The filtrate is examined for alumina, iron, calcium and magnesium in the usual manner.

Soluble Sulfates.—Treat 1 gram with 20 ml. conc. HCl, dilute to 200 ml. with hot water, boil, filter, wash, add NH_4OH until neutral, make acid with HCl and precipitate any sulfate as $BaSO_4$. Determine in the usual manner. Calculate to $CaSO_4$. If carbonates are present, calculate the remaining CaO to $CaCO_3$. Any excess of oxide is reported as CaO.

Carbon Dioxide.—Determine in the usual way. If any barium carbonate is present, it is determined in the filtrate from the preliminary HCl treatment, by precipitation and weighing, as $BaSO_4$. Any excess of carbon dioxide over the barium is reported as calcium carbonate.

ANALYSIS OF A COMPOSITE WHITE PAINT

A white paint may consist of a mixture of any of the preceding pigments, excepting that lead pigments and lithopone are seldom found together, owing to their tendency to blacken with the formation of lead sulfide.

After separation from the oil and other liquids as outlined above, the white pigment mixture may be rapidly analyzed by the following method. It is, however, often advisable to resort to a qualitative examination before beginning the quantitative analysis.

Insoluble Residue.—Boil 1 gram of the sample with 20 ml. (1 : 1) HCl. Evaporate to dryness, moisten the residue with a few ml. of concentrated HCl, allow to stand a few minutes, dilute with hot water, boil, filter and wash the insoluble residue thoroughly with hot water. Treat the insoluble residue with (1 : 1) HCl and 2 ml. H_2SO_4 to remove the last traces of lead. Filter, wash and weigh the insoluble residue. Determine the silica by volatilization with

H_2SO_4 and HF. Any loss is reported as silica. Determine the $BaSO_4$ in the residue by boiling with dilute HCl or by making a potassium bisulfate fusion. The residue remaining after either of these treatments is reported as barium sulfate.

Total Lead.—This constituent can best be determined on a separate sample. To 1 gram add 10 ml. of conc. HNO_3, boil, add, after cooling, conc. H_2SO_4 and evaporate to strong SO_3 fumes. Dilute with water, allow to stand several hours, filter, wash slightly, dissolve and determine the lead volumetrically as outlined under Sublimed White Lead.

Lead can also be determined on the combined filtrates from the insoluble residue. Precipitate the lead in an acid solution with H_2S and determine as directed under Basic Carbonate of Lead. Reserve the filtrate for the determination of iron, aluminum, zinc, calcium and magnesium.

To determine whether both sublimed white lead and corroded white lead are present, treat a separate portion of the paint with boiling acetic acid, filter and collect the insoluble residue. Determine the lead either in the filtrate or in the insoluble residue by the volumetric method. The lead soluble in acetic acid is the basic carbonate of lead and the lead oxide from the sublimed white lead, while the lead sulfate from the sublimed white lead remains insoluble.

Alumina and Iron Oxide.—Remove the H_2S from the filtrate from the lead sulfide, above, by boiling, oxidize the iron with a few drops of HNO_3, and precipitate the hydroxides with ammonia. Separate and determine the iron, and aluminum in the usual manner.

Zinc.—Acidify the filtrate from the alumina and iron precipitation with acetic acid, separate the zinc with H_2S and determine as outlined under Sublimed White Lead.

Calcium and Magnesium.—Determine the calcium and magnesium in the filtrate from the precipitation of zinc sulfide in the usual manner, first testing, however, for the presence of barium.

Sulfate.—Determine as outlined under Zinc Lead and Leaded Zincs.

Sulfide.—Should lithopone be present, separate the zinc oxide and zinc sulfide as outlined under Lithopone.

Carbon Dioxide.—Determine as outlined under Basic Carbonate of Lead.

Calculations.—Silica is reported as silica, except where alumina is present, showing the presence of China clay. In this case, calculate the alumina to clay by the following method.

Weight of $Al_2O_3 \times 2.5372 =$ weight of clay.

Weight of clay $\times 0.4667 =$ weight of SiO_2 in clay.

Any difference greater than 5% may be considered silica.

Barium sulfate is reported as barium sulfate or as lithopone, if zinc sulfide is present, according to the given composition of lithopone, 70% barium sulfate and 30% zinc sulfide.

Lead is reported as Basic Carbonate of Lead on the formula $2PbCO_3 \cdot Pb(OH)_2$.

Calculate lead soluble in acetic acid, after determining CO_2, to basic lead carbonate and any residual lead to lead oxide which, together with the lead sulfate is reported as Sublimed White Lead.

Should calcium sulfate be present, the portion soluble in water is examined for lime or sulfuric acid and calculated to calcium sulfate, any residual lime

being calculated to calcium carbonate and any residual sulfuric acid being calculated to lead sulfate. Any residual CO_2 after calculating calcium carbonate is calculated to white lead and any residual lead is calculated to lead oxide.

Lead oxide should not be reported except in the presence of lead sulfate. Any large percentage of magnesium indicates the presence of asbestine.

RED AND BROWN PIGMENTS

These pigments are grouped under these heads:

The Lead Oxide Pigments—The Iron Oxide and Manganese Oxide Pigments—The Mercury Oxide Pigments

RED LEAD AND ORANGE MINERAL

These pigments in the pure form are oxides of lead, of the generally accepted form, Pb_3O_4, being probably mixtures of lead monoxide, and lead dioxide.

Two methods are given for the analysis of this pigment.

Moisture.—Dry 2 grams at 105° for two hours.

Organic Color.—Boil 2 grams with 25 ml. of 95% ethyl alcohol, let settle, decant off the supernatant liquid; boil residue with water, decant as before and boil residue with very dilute NH_4OH. The pigment should also be extracted with chloroform. If either the alcohol, chloroform, water or NH_4OH is colored, organic coloring matter is indicated.

Total Lead and Insoluble Residue.—Treat 1 gram with 15 ml. of HNO_3 (1 : 1) and sufficient hydrogen dioxide to dissolve all the PbO_2 on warming. If any insoluble matter is present, add 25 ml. of water, boil, filter and wash with hot water. Insoluble contains free SiO_2, and should be examined for $BaSO_4$ and silicates, if appreciable. To the original solution or filtrate from insoluble, add 20 ml. of conc. H_2SO_4 and evaporate to SO_3 fumes; cool and determine lead as lead sulfate either gravimetrically or volumetrically. If the sample contains soluble barium salts, the $PbSO_4$ will contain $BaSO_4$ and should be treated with acid-ammonium acetate solution, the lead being determined in the filtrate.

Determination of Lead Peroxide (PbO_2) and True Red Lead (Pb_3O_4).—(Method of Diehl,[12] modified by Topf [13]—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given.)

Weigh 1 gram of finely ground sample into a 200-ml. Erlenmeyer flask, add a few drops of distilled water and rub the mixture to a smooth paste with a glass rod flattened on end. Mix in a small beaker 30 grams of C.P. "Tested Purity" crystallized sodium acetate, 2.4 grams of C.P. potassium iodide, 10 ml. of water and 10 ml. of 50% acetic acid; stir until all is liquid, warming gently; if necessary add 2 to 3 ml. of H_2O, cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved; add 30 ml. of water containing 5 or 6 grams of sodium acetate, and titrate at once with decinormal sodium thiosulfate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off rod, add the sodium thiosulfate solution until pale yellow, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of thiosulfate that had been added.

Calculation.—The iodine value of the sodium thiosulfate solution multiplied by $0.942 = PbO_2$; the iodine value multiplied by $2.700 = Pb_3O_4$; the PbO_2 value multiplied by $2.866 = Pb_3O_4$.

The red lead may also be examined for zinc, carbon dioxide, and soluble sulfate.

A second method for determination of the lead peroxide or true red lead content is somewhat shorter.[14]

Treat 1 gram in a beaker with 15 ml. of nitric acid, sp.gr. 1.2 (110 ml. nitric acid, sp.gr. 1.42 to 100 ml. of water). Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 ml. of dilute hydrogen dioxide (1 part of 3% hydrogen dioxide to 3.5 parts of water). Add about 50 ml. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 ml. volume and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen dioxide solution must now be made.

Into a beaker pour 15 ml. of nitric acid of above strength and add exactly the same amount of hydrogen dioxide (10 ml.). Dilute to 250 ml. with hot water and titrate with standard potassium permanganate solution to a faint pink color.

The difference between the number of ml. of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount required for the hydrogen dioxide which was reacted on by the

[12] Dingl. Polyt. Jour., **246**, 196.
[13] Zeitschrift für analytische Chemie, **26**, 296.
[14] "Analysis of Lead and Its Compounds," Schaeffer and White and Calbeck, p. 77.

red lead. The difference between the two amounts of potassium permanganate required multiplied by 3.058 grams gives the percentage of red lead present. The difference multiplied by 1.067 gives the percentage of PbO_2 present.

VERMILION

The following portion of Walker's [15] method will suffice for the examination of this pigment. Should the analyst desire to determine the sulfide of mercury present or make a more complete examination—reference may be made to the original method.

True vermilion, or, as it is generally called, English vermilion, is sulfide of mercury. On account of its cost it is rarely used in paints, and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulfur by extraction with carbon disulfide. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1%. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. Ash in a muffle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury.

Genuine vermilion is at the present time little used in paints. Organic lakes are used for most of the brilliant red, scarlet and vermilion shades. These organic coloring matters are sometimes precipitated on red lead, orange mineral or zinc oxide; but as a usual thing the base is barytes, whiting or China clay. Paranitraniline red, a compound of diazotized paranitraniline and beta-naphthol, is largely employed; but a number of colors may be used.

Paranitraniline red is soluble in chloroform. It is also well to try the solvent action on different reds, of sodium carbonate, etc. The amount of organic pigment present in such reds is generally very small, and when it cannot be determined by ignition owing to the presence of lead, zinc or carbonate, it is best determined by difference.

[15] P. H. Walker, Bulletin 109, Revised, Bureau of Chemistry, U. S. Dept. of Agri., pp. 31–33.

IRON OXIDES

The iron oxides and manganese oxide pigments include the ochres, umbers, siennas, Venetian red, metallic brown, Indian red and Tuscan red.

In analyzing these pigments, the following constituents are sought; moisture, loss on ignition, insoluble residue, iron oxide, manganese dioxide, calcium and magnesium oxides and sulfur trioxide.

Owing to the similarity of the methods used for the analysis of these pigments to those used in the analysis of iron ores, the analyst is referred to p. 469 on the Analysis of Iron Ores, or to the method of Walker.[16]

BLUE PIGMENTS

The principal blue pigments used in paints are Prussian, ultramarine, blue lead, and phthalocyanine.

Prussian blue is the double iron and potassium salt of hydroferrocyanic and hydroferricyanic acids.

Ultramarine blue is essentially a silicate and sulfide of sodium and aluminum.

Sublimed blue lead is the fume product resulting from the smelting of lead ores. In composition it consists of lead sulfate, lead sulfide, lead sulfite, lead oxide and zinc oxide, with occasional traces of carbon. It is finding its greatest use as an inhibitive pigment for the protection of iron and steel. Its color is a bluish gray.

Phthalocyanine blue is a copper compound of phthalocyanine and may be identified by the presence of copper.

ULTRAMARINE BLUE

Moisture.—Heat 2 grams at 105° C. for two hours.

Silica.—Digest 1 gram with 30 ml. of concentrated HCl, taking care to avoid spattering. Evaporate to dryness, dehydrate, moisten with conc. HCl, dehydrate a second time, dilute, filter, and determine the silica by volatilization with H_2SO_4 and HF.

Aluminum Oxide.—In the filtrate from the silica, precipitate the aluminum hydroxide and determine in the usual manner. Report as aluminum oxide.

[16] Bulletin 109, Revised, Bureau of Chemistry, U. S. Dept. Agri., pp. 33–34.

Sodium Oxide.—The filtrate from the aluminum hydroxide is acidified with H_2SO_4. Evaporate to dryness, ignite at a low red heat, and weigh the sodium sulfate. Calculate to sodium oxide.

Total Sulfur.—Fuse 1 gram with a mixture of KNO_3 and Na_2CO_3. Dissolve the fused mass in HCl, boil with conc. HNO_3 for one-half hour, remove the insoluble residue and determine the sulfuric acid in the usual way.

Sulfur Present as Sulfate.—Dissolve 1 gram in dilute HCl and boil until all the hydrogen sulfide is removed. Filter off the insoluble residue and determine the sulfate in the filtrate.

PRUSSIAN BLUE—(CHINESE BLUE)—ANTWERP BLUE

Moisture.—Heat 2 grams at 105° C. for two hours. Dry Prussian blue should contain less than 7% moisture.

Nitrogen.—Determine the nitrogen present by the Kjeldahl-Gunning method.

Iron and Aluminum Oxides.—Ignite 1 gram at a low temperature, sufficient to decompose all the blue, but not to render the iron difficultly soluble. Digest the residue with (1 : 1) HCl. Any insoluble residue is examined for silica, barium sulfate and alumina. A pure Prussian blue should show no insoluble residue. The filtrate is examined for alumina, iron and calcium in the usual way.

An aliquot portion of the filtrate after the removal of the calcium is examined for the alkaline metals. Calculate any alkaline metal present to sulfate.

Sulfuric Acid.—Determine the sulfuric acid in an aliquot portion after removal of the calcium.

Commercial Analysis.—The method of Parry and Coste [17] is sufficiently accurate to determine the Prussian blue in most instances.

If the pigment is a soda blue, the percentage of Prussian blue may be obtained with sufficient accuracy for commercial purposes by multiplying the percentage of nitrogen by 3.404 or the percentage of iron (in the absence of other iron pigments) by 2.8. The corresponding factors for potash blue are 4.4 and 3.03 respectively. Some blues, e.g., Chinese blue, may contain tin salts. Others may contain manganese or chromium compounds. The presence of these compounds should be determined by a qualitative examination at least.

[17] The Analyst, **21**, 225–230, 1896.

SUBLIMED BLUE LEAD [18]

Total Lead.—The total lead content is determined by the volumetric method for lead as outlined under Sublimed White Lead.

Total Sulfur.—Treat 0.5 gram with 10 ml. of water and a few ml. of bromine water. Boil gently until all the bromine has passed off. Dilute with water, add another portion of bromine water, boil, and continue the treatment until the sediment has become white in color. Add 8 ml. of nitric acid, evaporate until the brown fumes of nitric acid have disappeared, dilute with water and add an excess of sodium carbonate. Determine as outlined under Zinc Lead and Leaded Zinc.

Lead Sulfate.—On a separate sample determine the sulfate directly as outlined under Zinc Lead and Leaded Zinc, without any preliminary treatment for the oxidation of sulfites and sulfides.

Lead Sulfite.—Boil 1½ grams with 3 grams of sodium carbonate. Allow to stand, filter and thoroughly wash. Treat the filtrate with bromine water as outlined under Total Sulfur and determine the combined sulfur present as sulfate and sulfite. Deduct the amount present as sulfate and calculate to sulfite.

Lead Sulfide.—Deduct the sulfur present as sulfate and sulfite from the total sulfur and report the difference as lead sulfide.

Lead Carbonate.—Determine any CO_2 present by the evolution method and calculate to lead carbonate. See p. 235, Vol. I.

Lead Oxide.—Deduct the lead present as sulfate, sulfite, sulfide and carbonate from the total lead and report the difference as lead oxide.

Zinc Oxide.—Determine the zinc volumetrically as outlined under Sublimed White Lead and report as zinc oxide.

Carbon and Volatile Matter.—Ignite the sample in a partially covered crucible at a low heat for two hours. Report the difference in weight as carbon and volatile matter.

YELLOW AND ORANGE PIGMENTS

Chrome Yellows—American Vermilion—Basic Lead Chromate

The pigments under this class all contain chromates, with the exception of orange mineral, which is analyzed as under Red Lead. Frequently they contain lead sulfate and sometimes lead carbonate. A pure chrome yellow should contain only lead chromate and insoluble lead compounds. Owing to the

[18] "The Chemical Analysis of Lead and its Compounds," Schaeffer and White and Calbeck, p. 35.

frequent use of organic colors to brighten up the pigment, it is essential that a test be made for organic colors as outlined under Vermilion.

The analysis of these pigments is carried out in the following manner:

Moisture.—Heat 2 grams at 105° C. for two hours.

Insoluble Residue.—Treat 1 gram with 25 ml. of concentrated HCl, boil and during the boiling add a few drops of alcohol, one at a time. The solution is diluted to 100 ml., the boiling is continued for ten minutes and any insoluble residue is filtered off, thoroughly washed and examined for silica, barium sulfate and alumina.

Lead.—The solution is nearly neutralized with NH_4OH and the lead is precipitated as PbS with H_2S. Filter off the precipitate of PbS, dissolve in HNO_3, add H_2SO_4, boil to strong fumes and determine as outlined under Sublimed White Lead or weigh as $PbSO_4$.

Chromium.—The filtrate from the lead precipitation is boiled until all the H_2S is driven off. The solution is rendered alkaline with NH_4OH and the chromium is precipitated and determined as chromic oxide. Calculate to chromic anhydride.

If iron or aluminum is present, it will be necessary to separate the chromium by oxidizing it with Na_2O_2 to chromate, and then titrating it with ferrous sulfate.

Zinc, Calcium and Magnesium.—Precipitate the zinc in the filtrate with H_2S and determine as previously outlined.

In the filtrate from the zinc precipitation, determine the calcium and magnesium in the usual manner.

If any carbonates are present, determine by the evolution method.

Sulfuric Acid.—Determine the total sulfate as outlined under Zinc Lead and Leaded Zinc on p. 1861.

Calculations.—Any chromic anhydride is calculated to lead chromate, sulfuric acid to lead sulfate, if calcium sulfate is absent, and any residual lead is calculated to lead oxide.

GREEN PIGMENTS

Chrome Green

Green pigments are usually mixtures of chrome yellow and Prussian blue, though organic color is sometimes present, which may be determined by an extraction with alcohol or chloroform.

A microscopic examination should be made to determine whether the green is a combined precipitation product, which is of the greater value, or one mixed after separate precipitation. A good green will show the presence of green

and blue particles, while a poor green will show yellow and blue particles mixed with green. The analysis may be carried out as follows:[19]

Moisture.—Heat 2 grams at 105° C. for two hours.

Insoluble Residue.—Heat 1 gram at a low heat until the blue color has been decomposed, keeping the temperature sufficiently low so as not to render any of the iron or lead chromate insoluble. Determine the insoluble residue as outlined under Yellow Pigments.

Lead.—Determine as outlined under Yellow Pigments.

Iron, Alumina and Chromium.—All the H_2S is expelled from the filtrate after the lead precipitation by boiling. Add a few drops of HNO_3, boil a few minutes and precipitate the aluminum, iron and chromium hydroxides with NH_4OH. Filter, wash, dissolve the precipitate in HCl, and make up the solution to a definite volume.

In one portion the three hydroxides are precipitated together with NH_4OH and weighed. Another portion is treated in a flask with an excess of Na_2O_2 until the iron hydroxide has assumed its characteristic reddish-brown color. Dilute with water, filter, wash and determine the iron in the usual way. Render an aliquot of the filtrate from the iron precipitation acid with HNO_3, precipitate the aluminum hydroxide with NH_4OH and weigh as Al_2O_3.

Chromium is determined in the filtrate by titration with ferrous ammonium sulfate as described under Yellow Pigments. Any method for the separation of the above hydroxides may be used in place of the one outlined.

Calcium and Magnesium.—These constituents are determined in the filtrate from the precipitation of the above hydroxides.

Sulfuric Acid.—One gram after ignition until all the blue has been decomposed, is dissolved in 30 ml. of conc. HCl, diluted with water, boiled, filtered, and washed. The sulfuric acid is determined in the filtrate.

Nitrogen.—Determine as outlined under Prussian Blue.

Calculation.—The Prussian blue is determined by using the factors given under Prussian Blue. The sulfate is calculated to lead sulfate and calcium sulfate, should calcium be present, and the chromium to lead chromate.

BLACK PIGMENTS

The black pigments include those which contain carbon as their essential constituent. The introduction of many black pigments which are made from asphaltic and coal-tar mixtures complicates their chemical analysis. For those pigments which contain coal-tar mixtures, recourse may be had to works[20] covering this matter thoroughly.

[19] "The Analysis of Paints," Gardner and Schaeffer, pp. 36–37.

[20] Allen's "Commercial Organic Analysis," 4th Edition; "The Analysis of Paints," Gardner and Schaeffer.

The analysis of the simple black pigments may be carried out in the following way:

Moisture.—Dry 2 grams at 105° C. for two hours.

Oil.—Extract 2 grams, with ether in a fat-extraction apparatus.

Carbon.—Determine the carbon by difference after determining the moisture, oil and ash.

Ash.—Ignite 2 grams to a bright red heat until all the carbon is driven off. If graphite is present, the ignition must be carried out with the aid of oxygen. Should carbonate be present, mix the ash with a small amount of ammonium carbonate and again ignite, thus reconverting to carbonate any oxide which may have been decomposed.

Analysis of Ash.—The ash is boiled with concentrated HCl and the insoluble residue determined in the usual manner. The filtrate is examined for calcium, magnesium and phosphoric acid.

Calculate the magnesium to phosphate, any residual phosphoric acid to calcium phosphate and any residual calcium to carbonate.

PAPER AND PAPER-MAKING MATERIALS

STANDARD METHODS OF THE TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY [1]

ISOLATION OF CELLULOSE BY CHLORINATION METHOD [2]

Apparatus.—A special chlorination apparatus as illustrated in Fig. 266 is required for this determination. It consists of one leveling tube and holder, two individual glass 3-way stopcocks, one thermometer, one Hempel precision gas burette fitted with a 3-way stopcock, a glass water jacket for the gas burette, one Hempel gas pipette, several Jena glass crucibles (No. 3, 35 ml. capacity) equipped with a fritted glass bottom of porosity 5 to 7. In addition, alundum crucibles with about the same capacity and of porosity R. A. 98 are required.

Solutions.—*Alcohol-benzene:* This solution consists of 33% alcohol and 67% benzene by volume.

Calcium Chloride Solution for Gas Burette and Gas Pipette.—Saturate water with $CaCl_2$ at room temperature, bubble chlorine gas in until saturated and filter for use. When the apparatus is not in use it is well to have it filled with fresh Cl gas, thus keeping the $CaCl_2$ solution saturated.

Test Specimen.—The specimen shall consist of about 2 grams of a representative sample of air-dry disintegrated wood or pulp of known moisture content.

The samples of wood or pulp for analysis shall be prepared according to the procedures described in the official methods.

Procedure.—Weigh accurately approximately 2 grams of air-dry wood or pulp in a tared alundum crucible contained in a weighing bottle. Extract the crucible with contents, in the case of wood (the extraction may be dispensed with in the case of pulps), for 6 hours, or over night if more convenient, in a Soxhlet extractor with the mixture of alcohol and benzene. After evaporation of the solvent wash the sawdust thoroughly with hot water, using the suction pump. Then transfer the moist material to a Jena glass crucible. The crucible is water jacketed and connected between the gas burette and the gas pipette, as shown in Fig. 266, by means of two rubber stoppers through which passes a capillary glass tubing. Apply suction first at the bottom of the crucible until the excess moisture is removed, and then at the top. The latter removes the water from the fritted glass plate and evenly distributes the remaining moisture throughout the entire sample.

Pass a burette-full of chlorine gas from the burette up through the material in the crucible and over into the gas pipette as fast as possible. The tem-

[1] Reproduced with the permission of the Technical Association of the Pulp and Paper Industry.

[2] T 201 m. Tentative Standard—Sept. 11, 1930. Official Standard—Aug. 15, 1932. Corrected—March 15, 1934.

perature of the water in the water jacket should be in the range of 23.5° to 32° C., inclusive. During the first chlorination samples of wood absorb approximately 230 ml. of Cl gas at room temperature and atmospheric pressure. This necessitates refilling the burette, which may be done quickly as it is connected to a Cl tank with a 3-way stop cock. The first chlorination treatment requires from 3 to 4 minutes, after which remove the crucible from the apparatus and wash the material with approximately 50 ml. of distilled water, and successively with 50 ml. of approximately 3% SO_2-water, 50 ml. of water, then 50 ml. of freshly prepared 2% sodium sulfite solution. Transfer the material to a 250-ml. Pyrex beaker, using a pointed glass rod. The last traces of material are washed out of the crucible with 100 ml. of 2% Na_2SO_3 solution with the aid of a rubber policeman drawn gently over the bottom of the crucible.

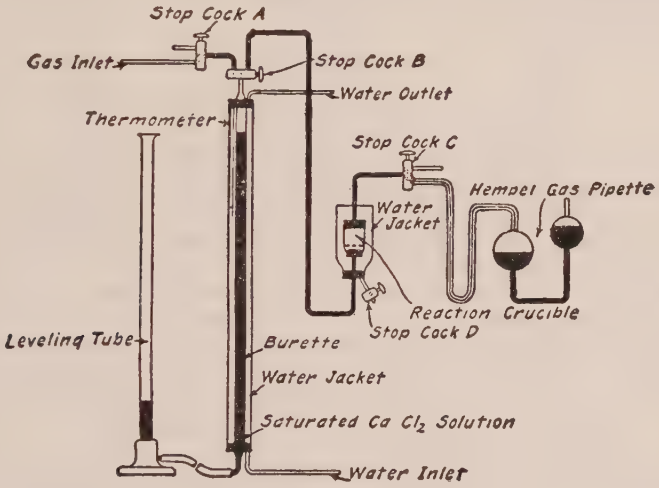

Fig. 266.—Apparatus for Isolation of Cellulose.

Approximately 15-ml. portions of the Na_2SO_3 solution are added to the crucible for each washing. When 60 ml. have been thus used, place 10-ml. portions of the remainder in a watch glass and by means of applying gentle suction to the top of the crucible, placed on the watch glass as before described, remove all of the material from the fritted glass bottom of the crucible. Cover the beaker containing the sample with a watch glass and place in a boiling water bath for 30 minutes. Again transfer the fibers to the glass crucible and wash with about 250 ml. of distilled water.

The above procedure is never sufficient to remove all the lignin, so that the treatment with Cl and subsequent treatments as outlined above must be repeated until the fibers show only a very faint tinge of pink upon addition of the Na_2SO_3 solution. The second and following treatments with Cl should not require more than 2 or 3 minutes. Prolonged action of Cl gas, together with the HCl formed in the secondary reactions, hydrolyze the cellulose, give low yields and cause varying amounts of alpha-cellulose.

After all of the lignin has been removed, wash the fiber thoroughly in the alundum crucible successively with 500 ml. of hot water, 50 ml. of 95% alcohol and finally with 50 ml. of ether. Then dry it for 2½ hours at 105° C. in an electrically heated oven.

Finally place the tared alundum crucible in the original stoppered weighing bottle, cool in a desiccator over conc. H_2SO_4 and weigh as cellulose.

Report.—The weight of the residue shall be reported as a percentage of the oven-dry weight of unextracted material.

Additional Information

Roe, J. Ind. Eng. Chem. **16**, 8 (1924).
Bray and Andrews, Paper Trade J. **76**, No. 8 (1923).
U. S. Forest Products Laboratory Standard Testing Manual for Pulpwood, Pulp, Stuff, and Paper.
Bray, M. W., Paper Trade J. **87**, No. 24 (1928).

CHLORINE CONSUMPTION OF PULP[3]

This value, obtainable during the isolation of cellulose, is a measure of the amount of chlorine gas actually consumed by compounds other than cellulose in the pulp. Such values for a series of pulps indicate the relative bleachabilities of the pulps and with a sufficient background of data can be used to predict actual bleachabilities.

Apparatus.—The special chlorination apparatus as described in the standard method for the isolation of cellulose is required. (See Fig. 266.)

Specimen.—The specimen shall consist of about 2 grams of a representative sample of air-dry disintegrated pulp of known moisture content.

Procedure.—The procedure used for the isolation of cellulose shall be followed as described, together with certain additional steps:

Run about 90 ml. of Cl gas into the gas burette and note the exact amount, after which pass the entire amount of gas up through the sample and over into the gas pipette.

NOTE.—This method is a revision of U. S. Forest Products Laboratory Official method No. 35 [See Paper Trade J. **87**, 25, 52–53 (1928)].

Then run the unconsumed gas back into the gas burette and note the exact amount. By difference, obtain the total volume of gas used. When the Jena glass crucible containing the chlorinated sample is placed in the suction filter flask, wash the pulp with four 25-ml. portions of water at a temperature of 18–23° C. Keep this filtrate in a properly labeled and covered beaker.

At each successive chlorination repeat the above procedure and correct the total volume of Cl used to standard conditions of temperature and pressure, i.e. 0° C. and 760 mm., taking into consideration the vapor pressure of water vapor at the chlorination temperature over a saturated $CaCl_2$ solution saturated with Cl gas. This calculation is made by means of the following formula:

[3] T 202 m. Tentative Standard—Sept. 11, 1930. Official Standard—Aug. 15, 1932. Corrected—May 15, 1935.

$$V_0 = \frac{V_1 \times (p - a)}{760(1 + 0.00367t)}$$

Where V_1 = volume of gas observed at t deg. C.
V_0 = volume under standard conditions.
a = vapor pressure of water vapor over saturated $CaCl_2$ solution saturated with Cl gas, in mm. mercury at t deg. C.
t = the temperature of chlorination in deg. C.
p = observed barometric pressure in mm. of mercury.

The following table is of assistance in making these calculations.

t° C.	a	760 × (1 + 0.00367 t)
23.5	15.9	826.00
24.0	16.6	826.90
24.5	17.3	828.36
25.0	18.0	829.76
26.0	19.4	832.57
26.5	20.0	833.80
27.0	20.8	835.40
28.0	22.0	838.12
29.0	23.5	840.96
30.0	25.0	843.66
31.0	26.4	846.48
32.0	29.0	849.30

The weight of 1 ml. of Cl gas at standard temperature and pressure = 0.003164 gram.

Titrate the combined initial wash waters with standard alkali to determine the weight of Cl gas that formed HCl. Then determine by difference the weight of Cl actually consumed by the pulp.

Report.—The data shall be reported as the percentage of Cl consumed, calculated on the oven-dry weight of the sample.

ALPHA CELLULOSE IN PULP[4]

This method as described is an attempt to formulate a procedure which is accurate and sufficiently simple so that it may be used as a routine test. The method herein described is adapted from the tentative standard Method IV of the American Chemical Society [5] and is the most successful method investigated by the Division of Cellulose Chemistry of that Society. It is applicable to paper making fibers provided they are not highly lignified.

NOTE.—For the determination of alpha cellulose in paper see T 429 m.

Test Specimen.—The usual precautions for sampling pulp should be rigidly followed. The sample shall be in an air-dried condition, in an open, fluffy form, prepared by being brushed apart while dry by means of a disintegrator of the Gosta Hall or Koerner type. It shall be stored in an air-tight glass-stoppered container or fruit jar for at least 48 hours to attain a uniform mois-

[4] T 203 m-36. Tentative Standard—Feb. 19, 1931. Revised—Feb. 17, 1932. Official Standard—Aug. 15, 1932. Corrected—Sept. 15, 1936.
[5] (Ind. and Eng. Chem., Anal. Ed. **1**, 54 (1929)).

ture content throughout the material. Samples for moisture content and alpha cellulose determinations shall be withdrawn as needed.

Reagent.—*17.5% NaOH Solution.*—The sodium hydroxide solution is prepared by dissolving solid NaOH in an equal weight of water, and allowing it to stand until the Na_2CO_3 and other impurities have settled, leaving a clear supernatant liquid. The clear liquid is decanted and diluted with CO_2-free water until its density at 15° C. is 1.197. Such a solution contains 17.5±0.1 grams of sodium hydroxide per 100 grams of solution.

Procedure.—Weigh accurately in triplicate about 3 grams in a weighing bottle and transfer to a 250-ml. Pyrex beaker. Add 35 ml. of 17.5% carbonate-free NaOH solution and allow the whole to stand for 5 minutes. Macerate the pulp for 10 minutes with a short rod which has the end flattened to a disk 1 cm. in diameter. During this maceration add 40 ml. of 17.5% NaOH solution at 20° C. intermittently in 10-ml. portions. Then cover the beaker with a watch glass. After 30 minutes additional mercerizing action in a water bath at 20° C. (total mercerization time 45 minutes) add 75 ml. of distilled water (at 20° C.) to the alkali-cellulose mixture with thorough stirring. Filter the contents of the beaker immediately by means of suction on a 40-ml. Gooch crucible having a finely perforated bottom, allowing the cellulose to form its own mat. Pour the filtrate through the mat a second and third time, if necessary, to catch any fine material. Wash the residue in the Gooch crucible with exactly 750 ml. of distilled water (at 20° C.) by means of suction. Disconnect the suction tube, add 40 ml. of 10% acetic acid (at 20° C.) and allow to soak for 5 minutes. Then apply suction to remove the acid. Wash the alpha cellulose with distilled water until free from acid. Carefully remove it from the Gooch crucible to a tared, flat, glass-stoppered weighing bottle. Dry the unstoppered bottle and contents to constant weight at 105° C., making the first weight at the end of 6 hours and then at 1-hour intervals until constant. Let the weighing bottle and its contents cool in a desiccator for 30 minutes and cover before weighing.

Note.—Drying of the alpha cellulose can be greatly expedited if the last washing is followed by 95% ethanol and then by ether or some other highly volatile non-reactive liquid. In each case the washing fluid is allowed to soak into the sample for several minutes before being removed by suction. In this way the time in the oven at which constant weight is reached may be reduced to about 2 hours instead of 6 hours or more. The results of the two drying methods check each other within the limits of experimental error.

Determine the ash content of one of the triplicate alpha-cellulose residues in the usual manner, and use the other residues (in the case of unbleached pulps) for the determination of residual lignin, as below.

Modification for Unbleached Pulps.—In the case of unbleached chemical wood pulps, correct the alpha cellulose figure for lignin remaining in the residue after mercerization by the following procedure adapted from the method developed by the U. S. Forest Products Laboratory, Madison, Wis.: [6]

Treat the residue from the mercerization test with 5 ml. of water in the original weighing tube in which it was weighed; stopper, and allow to stand over night at room temperature. Then remove the residue to a beaker and

[6] (Paper Trade J. 87, 61 (1928)).

treat with 45 ml. of H_2SO_4, sp.gr. 1.695 (76.76% by weight), at 15° C. and let the digestion proceed at 25° C. for 16 hours. Transfer the mixture to a 2-liter Erlenmeyer flask, dilute with 1570 ml. of water, cover with a watch glass and boil for 2 hours, maintaining a constant level by the addition of boiling water. Filter the residue through a tared Gooch or sintered glass crucible, wash with hot distilled water and dry to constant weight at 100–105° C. Correct the alpha cellulose figure by subtracting the percentage of lignin residue thus obtained.

NOTES.—(*a*) *Time interval for steps in the procedure:* An interval of 15 minutes should elapse between the times of starting the alkali treatment of the individual triplicate samples. Such a procedure allows time before proceeding to the next sample in a triplicate determination for the various steps in the procedure, such as impregnation, maceration, filtration, and partial washing.

If 5 minutes are allowed between the addition of a part of the alkali and the beginning of maceration, it will be found that sulfite pulp swells to five or six times its original volume, and the fibers can be much more easily macerated. The remaining 10-minute interval, during which the remaining 40 ml. portion of the alkali is added, making a total of 75 ml. has been found ample time for the maceration of pulps. With such a scheme, for example, one would add the alkali to the samples at 9:00 o'clock, 9:15, and 9:30, respectively. Filtering would begin at 9:45 o'clock, 10:00, and 10:15, respectively.

(*b*) *Filtering Medium:* Jena glass filter crucibles (coarse) may be used in place of the Gooch crucibles specified in the directions.

(*c*) *Testing for acidity:* To test the acidity of the wash water on litmus paper, the last few drops removed after the addition of water should be used.

Report.—Report results on the oven-dry basis to tenths of a per cent.

Precision.—Duplicate samples should check each other to within 0.2.

PITCH IN WOOD PULP[7]

Preparation of Sample.—If the pulp is sufficiently wet, it shall be separated into thin layers and allowed to dry in the air overnight. If the pulp is too dry for this, it shall be soaked in water, then separated into layers and allowed to dry overnight. The layers shall then be cut into pieces about 2×4 inches and 5 grams weighed out for each extraction. Pieces shall be creased alternately parallel to the shorter direction so that they may be closed up like a camera bellows. This is very necessary to keep the surfaces apart in the extractor and facilitate rapid extraction. (If preferred, the pulp may be shredded before extraction and packed into the extractor loosely.)

Where extreme accuracy is desired the moisture shall be determined on a separate portion of the air-dried pulp by drying a weighed sample to constant weight at 100–105° C., and the pitch percentages subsequently obtained shall be corrected to the air-dry basis by dividing the actual results by $\frac{1-X}{0.90}$, where X is the percentage of moisture expressed as a decimal. For ordinary purposes, however, the strips dried overnight may be considered in the air-dry condition.

[7] T 204 m. Tentative Standard—Dec. 31, 1931. Official Standard—March 1, 1933. Corrected—May 15, 1935.

Ether Extract.—Accurately weigh 5 grams of the pulp prepared as previously described, place it in a Soxhlet or a continuous extractor, connected to an unweighed Erlenmeyer or Soxhlet flask, and extract with sulfuric ether for at least 16 hours with the ether boiling rapidly.

Filter the ether solution through a wad of absorbent cotton in the bottom of a glass funnel, washing the funnel and the cotton finally with a little ether, and collect the filtrate in a weighed Soxhlet flask. Then evaporate the solution in the flask, dry the residue on the steam bath until the ether is removed and finally dry in the oven at not over 105° C. to constant weight. Calculate the weight of residue to percentage of the air-dry pulp and report as ether-soluble pitch.

Alcohol Extract.—After completion of the ether extraction place another unweighed flask under the extractor and extract the pulp sample with neutral ethyl alcohol (specially denatured alcohol-No. 30 may be used) for at least 16 hours in a Soxhlet or a continuous extractor. Filter the alcohol solution through cotton into a weighed flask as previously described, evaporate the alcohol, dry the residue on the steam bath and then to constant weight at not over 105° C. in the oven. Calculate the weight of extract to percentage of the air-dry pulp and report as alcohol-soluble pitch (insoluble in ether).

NOTE.—In the case of sulfite pulp time may be saved by extracting a separate portion of the prepared sample directly with alcohol to obtain the total pitch. In this case the difference between the percentage of total pitch and of ether-soluble pitch is the alcohol-soluble pitch insoluble in ether.

Total Pitch.—The total pitch shall be reported as the sum of the percentages of the ether-soluble pitch and the alcohol-soluble pitch insoluble in ether.

NOTE.—E. Richter [8] and E. Opfermann [9] were among the first to call attention to the fact that the pitch in sulfite pulp is completely soluble in alcohol and a portion of it is soluble in ether. Opfermann pointed out that by extracting sulfite pulp first with ether and subsequently with alcohol the sum of the two extracts is the same as the total extract obtained by alcohol alone and he further expressed the opinion that it is the ether-soluble portion of the pitch that causes the most trouble in paper making. In such cases as the writer [10] has been able to follow through, it has been found that unbleached sulfite pulp causing pitch troubles in making tissue paper showed an ether extract greater than 1%. As there seems to be still some question as to whether it is the total pitch in the pulp or the ether-soluble pitch which gives trouble, it seems generally advisable to determine both forms of pitch.

CUPRAMMONIUM DISPERSE VISCOSITY OF PULP [11]

The following detailed directions for the determination of cuprammonium viscosity of pulps is an attempt to formulate a simple procedure which is sufficiently accurate and reproducible that it may serve as a routine test.

[8] C. A. 8, 2803 (1914).

[9] Z. für Angew. Chem. 22, 436 (1909).

[10] This note was written in 1931 by R. C. Griffin who was at that time chairman of the Non-Fibrous Materials Testing Committee.

[11] T 206 m. Tentative Standard—Feb. 14, 1932. Official Standard—April 15, 1933. Tentative Revision—April 15, 1935. This revision has been approved by the Pulp Testing Committee. Send comments to R. G. Macdonald, 122 E. 42nd Street, New York, N. Y.

The method herein described is a modification of the Shirley Institute method (1). This procedure has been found applicable to bleached and unbleached chemical pulps and to rag stocks.

Apparatus.—*Viscosity Tube.*—The viscosity tube shown in Fig. 267 is used both for dissolving the pulp and for determining the viscosity of the solution. The tube, of heavy Pyrex glass, has an internal diameter of 1.0 cm. and a total length of 27 cm. The capillary is 2.5 cm. long and 0.09 cm. inside diameter. The wide portion is etched with three rings, A, B, and C, at heights 24.2, 12.2, and 6.2 cm. above the flat end of the capillary. (The mark at B is optional, to be used with hard unbleached pulps. In this case the constant for the tube between the marks A and B should also be determined.)

The applicability of the procedure to pulps of widely varying viscosities is greatly improved by using tubes of different efflux rates for different pulps. The following efflux rates determined with distilled water at 20° C. are specified:

	Seconds
Bleached pulp	15–25
Unbleached pulp and high viscosity rag stock	10–15

FIG. 267. Viscosity Tube.

These specifications are in addition to those for the dimensions and do not alter the dimensions.

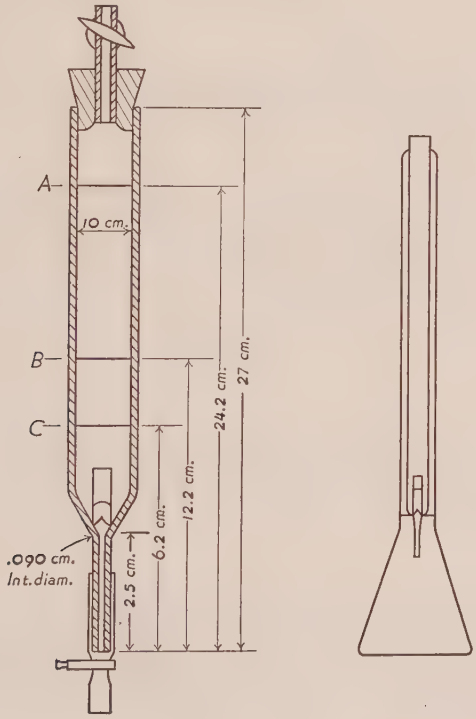

FIG. 268.—Jacket.

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The top of the tube is closed with a rubber stopper, carrying another capillary which has a ground-glass stopcock. The bottom capillary is closed with a rubber tube and clamp. Each tube has a wedge-shaped cylinder, Fig. 269, the bottom of which is notched. The cylinder, made from ¼-inch steel or Monel rod, is 2.5 cm. long.

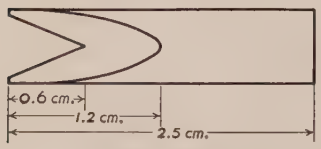


FIG. 269.—The Wedge.

The glass jacket, Fig. 268, supports the viscosity tube in the thermostat. The jacket is so constructed that it supports the tube on three glass points at the bottom and is a sliding fit at the top.

Calibration of Viscosity Tube.—The volume of the tube is obtained as follows: Fill the tube, containing the wedge, with water, put the rubber stopper [12] tightly in place and force the excess water out through the capillary. Open the stopcock and drain the contents into a burette, noting the time in seconds for the meniscus to fall from line *A* to line *C*. Read the volume of the water delivered to the burette and take the average of several determinations as the volume of the tube.

The tube constants *C* and *k* are determined from the formula:

$$V = \frac{d}{C}\left(t - \frac{k}{t}\right), \tag{1}$$

where V = viscosity in centipoises;
d = specific gravity of the solution;
t = time in seconds for meniscus to fall from line *A* to *C*;
C = tube constant;
and k = gravity constant.

The constant *C* is first determined with standard glycerine solution of approximately 1.21 sp.gr. (85% glycerine solution) at 20.0° C. (The sp.gr. of the glycerine solution must be accurately determined with a pycnometer.) The viscosity of the glycerine solution may be obtained from a curve drawn from Table I. In this case constant *k* may be disregarded, since the time of efflux is long. The formula then becomes

$$C = \frac{dt}{V}, \tag{2}$$

from which the tube constant is calculated. The gravity constant *k* is determined by repeating the operation with water at 20.0° C. and substituting for *C* in formula (1) the value found above, as well as $d = 1$ and $V = 1$. The formula then becomes

$$k = t^2 - ct. \tag{3}$$

Reagent.—***Cuprammonium Solution.***—Freshly prepare the cuprammonium solution at least every 2 months as follows: Place clean copper turnings in a glass tube 24 inches long and 4 inches in diameter, surrounded with ice. (The

[12] The rubber stopper must be replaced periodically by a fresh one, determining the new volume each time.

turnings must be previously cleaned by washing in dilute HCl.) Pour in conc. NH_4OH (26–28% NH_3) containing 2 grams of cane sugar per liter until the tube is nearly full. Bubble air, which is passed through a wash-bottle containing conc. NH_4OH, through the solution for several hours, until the desired Cu concentration is reached. Analyze the solution for Cu and NH_3, and make the proper adjustments. The Cu concentration shall be 14.8–15.2 grams per liter, the NH_3 concentration 190–210 grams per liter.

The course of the reaction can be followed by estimating the Cu content colorimetrically by comparing with a standard, both diluted 50-fold.

Determine the Cu and NH_3 in the cuprammonium solution as follows:

(*a*) *Copper:* Pipette 10 ml. of the cuprammonium solution into a 250-ml. Erlenmeyer flask, and dilute with 25 ml. of water. Boil the solution until no more NH_3 is given off. Add 5 ml. of HNO_3 (1 : 1) and boil till red fumes are expelled. Then add 2 ml. of bromine water and boil until the Br is all expelled. Remove from the heat, dilute to 75 ml. and carefully add NH_4OH until the solution becomes just alkaline (blue) but not more. Add a slight excess (4 or 5 ml.) of glacial acetic acid, cool to tap water temperature, and add 10 ml. of 30% KI solution. Titrate with 0.1 N thiosulfate solution until the yellow color of free iodine is nearly gone, then add starch indicator and continue the titration cautiously until, on the addition of another drop, the blue color due to free I disappears.

Calculation: Copper content of cuprammonium solution in grams per liter = ml. 0.1 N thiosulfate × 0.636.

(*b*) *Ammonia:* Pipette 2 ml. of the cuprammonium solution into 50 ml. of normal H_2SO_4 solution, keeping the tip of the pipette beneath the surface of the liquid. Titrate the excess acid with normal NaOH, using methyl red indicator.

Calculation: NH_3 content of cuprammonium solution in grams per liter = (50—ml. NaOH) × 8.5—0.536 *C*.

Where *C* = copper concentration in grams per liter.

Care should be taken that no liquid adheres to the outside of the pipette before it is inserted into the acid solution. The correction factor (0.536 *C*) is made for the alkalinity of the copper hydroxide.

Test Specimen.—A representative pulp sample in the air-dry condition shall be shredded by means of a mechanical shredder or a coarse steel file. Wet pulp may be made into several handsheets, dried in the oven at 100° C. for 3 minutes, and then shredded.

The air-dry pulp shall be placed in a stoppered bottle and the moisture content determined on a portion of it. The weight of air-dry pulp equivalent to 1 gram of oven-dry pulp for each 100 ml. of tube volume shall be calculated for each tube and the proper amount of sample weighed out for the tube employed.

Procedure.—Take the calculated weight of oven-dry pulp to give a 1% solution and loosely roll it into the form of a cigarette in a strip of hard-surfaced paper such as glassine; then moisten this roll with 5 or 6 drops of water and slide it from the paper into the viscosity tube. Siphon the cuprammonium solution into the bottom of the tube by means of the rubber tubing at the

bottom, until it is two-thirds full. Quickly break up the pulp roll with the aid of a thin glass stirring rod. Add the remainder of the solution at the top, scrape the rod clean and insert the stopper. Force the excess solution through the capillary and close the stopcock. Wrap the viscosity tube in black cloth; and place it on a wheel rotating 3 or 4 r.p.m., so that the metal wedge falls freely through the solution as the tube rotates. The pulp should be well broken up so that the metal wedge will fall through the full length of the tube, before the tube is put on the rotating wheel. Allow 15 hours rotation (over night) for the complete dispersion of the pulp.

Place the tube in the thermostat at 20° C. till equilibrium is established. Remove the rubber tubing from the capillary and place the tube in position in the jacket, which remains in the thermostat. Remove the rubber stopper, allowing the pulp solution to flow through the capillary. Note the time in seconds (t) for the meniscus to pass between the marks A and C, and calculate the viscosity of the solution from the formula:

$$V = \frac{d}{C}\left(t - \frac{k}{t}\right),$$

in which d, the sp.gr. of the pulp solution, is 0.96; C and k are constants found. Simplifying, the equation becomes:

$$V = C_1\left(t - \frac{k}{t}\right), \qquad \text{where} \qquad C_1 = \frac{0.96}{C}.$$

Inspection will show when the expression k/t may be disregarded, as is usually the case with unbleached pulps of high viscosity.

The tubes may be cleaned by immersion in nitric acid (1 : 1).

Report.—Results shall be reported in terms of centipoises and represent the average of at least two tests.

Precision.—Duplicate samples should check within 2.0% on bleached, and 3.0% on unbleached pulps.

TABLE I.—VISCOSITY OF GLYCERINE-WATER SOLUTIONS

(International Critical Tables, Vol. 5, p. 23)

Specific Gravity at 20.0° C.	Viscosity in Centipoises at 20.0° C.
1.0000	1.009
1.1014	3.734
1.1699	15.360
1.1848	23.540
1.2057	49.670
1.2155	74.780
1.2240	110.800
1.2463	409.300
1.2568	871.700

Literature Cited

1. Clibbens and Geake, "The Measurement of the Fluidity of Cotton in Cuprammonium Solution," J. Textile Inst., **19**, 77–92 T (1928).
2. Committee Report of Am. Chem. Soc., Ind. Eng. Chem., Anal. Ed. **1**, 49–51 (1929).

MOISTURE IN PULP BY TOLUENE METHOD[13]

This method is a rapid and accurate procedure for the determination of moisture in comparatively small laboratory samples, but is not intended to be used in place of T 210m in acceptance tests of pulp shipments. Since the method does not include as water any other volatile impurities such as turpentine, unless they are soluble in water, it is especially valuable for ground wood pulp.

Apparatus.—The apparatus required is as follows: (1) a balance with a capacity of about 1 kilogram and a sensitivity of at least 0.1 gram; (2) a Liebig condenser with a jacket length of at least 24 inches; (3) a straight drying tube charged with anhydrous $CaCl_2$; (4) a moisture trap; (5) an accurately graduated and calibrated cylinder of 100-ml. or 50-ml. capacity; (6) a 2-liter Pyrex short-necked balloon flask; (7) a source of heat, preferably an electric heater, although a Bunsen burner is adequate; (8) cork stoppers and rubber tubing for connections; (9) iron supporting stand and clamps.

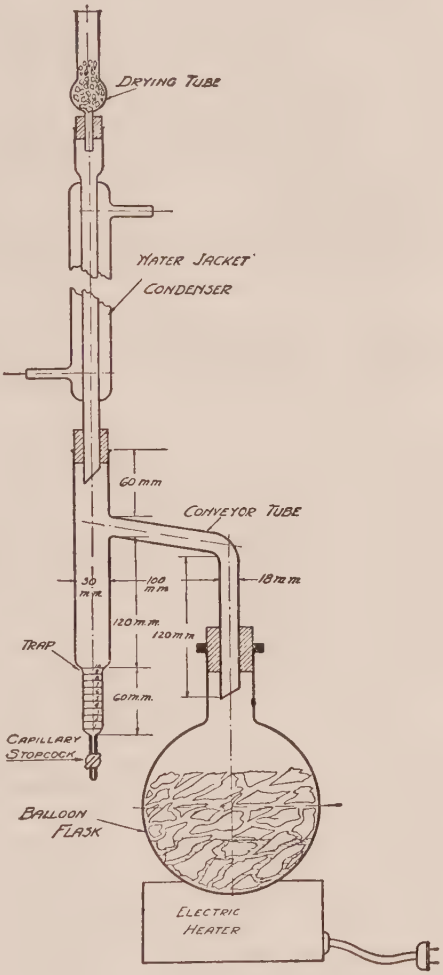


FIG. 270.—Apparatus for the Determination of Moisture in Pulp.

The moisture trap follows the general plan of that used in the Dean-Stark water determination apparatus[14] but with certain modifications. It is considerably larger than the 10-ml. size ordinarily used and should hold about 100 ml. The exact size is not important. The lower portion only is graduated and is of smaller diameter than the upper part, since the boundary meniscus between toluene and water in a glass tube is much more rounded and harder to reproduce in the same shape each time than is the air-water meniscus. A glass stopcock is sealed on at the bottom to permit drawing off the water for measurement. The other apparatus is of the ordinary type and needs no particular description. The drying tube at

[13] T 208 m. Tentative Standard—Feb. 16, 1932. Tentative Revision—April 6, 1933. Official Standard—March 15, 1934.

[14] Obtainable at any chemical apparatus supply house.

the top of the condenser is necessary to prevent condensation of moisture from the atmosphere if the humidity is high. This assembly is shown in Fig. 270.

Reagent.—***Toluene.***—The toluene should be reasonably pure, preferably colorless, clear and free from visible water droplets. It is unnecessary to dry it, especially if the above conditions are met. It may be used over again if redistilled and dried to the above specifications. It is unnecessary for the sample in the flask to be covered by the toluene. The amount of toluene for each determination (500 ml.) need only be measured approximately.

Test Specimen.—Pulp samples should be collected in accordance with the present standard methods for pulp sampling and should at once be placed in airtight containers (cans or jars) neither heated nor cooled, and analyzed as soon as possible.

The samples should not exceed about ½ pound in weight for each determination. If, as in the strip or wedge method of pulp sampling, they must greatly exceed this, then separate determinations should be made.

NOTE.—Where samples are very large and must be so in order to get accurate sampling, the method is applicable by breaking up the large samples into several smaller ones or by using a 5-liter flask containing 1000 ml. of toluene. If this requires more laboratory attention than is available, the drying method must be resorted to.

Procedure.—Weigh the closed jar or can containing the sample to the nearest 0.1 gram, cover and all. Then open and transfer about 100 to 300 grams of the pulp to the flask (which already contains 500 ml. of toluene) as rapidly as possible. Replace the cover on the container and again weigh. Connect the apparatus, turn on the cooling water and boil the toluene until no more water collects. Either during the boiling or at the end, if the trap does not become completely filled with water, draw off the water through the stopcock into an accurately graduated cylinder, cool to below 30° C. and measure its volume.

When draining the water from the apparatus into the measuring cylinder, allow time for the water to drain from the walls and drain the last portions of water into the cylinder by touching its lip to the draining tube until all water is removed.

Since a 100-ml. cylinder is graduated only to about 1 ml., a more accurate measurement can be made, for smaller amounts of water, by using a 25-ml. or 50-ml. graduated cylinder or a burette. If the amount of water is small, due either to a small sample or a very dry sample, it need not be drained off but can be measured on the graduations at the bottom of the trap. The cylinders should be accurately calibrated for use, both for water alone and for water with a toluene layer above it. It sometimes happens that a few drops of toluene remain in the tube at the bottom of the trap and when the water is drawn off this toluene is also removed. Since the water meniscus is of a different shape with air than with toluene, the graduate should be calibrated for both conditions. Trap and graduates may be calibrated as follows:

Set the dry, clean trap or graduate in a vertical position, run in water from an accurate burette up to the first test interval graduation (5 or 10 ml. for the graduates, 1 ml. for the trap) and read the burette. This is then repeated for each interval used. The operation should also be repeated with 5 ml. of

toluene in the trap or graduate. The calibration is conveniently represented by graphs showing reading along one axis and actual volume along the other.

To minimize the difficulties due to the meniscus assuming different shapes, the tubes should be cleaned frequently with hot chromic-sulfuric acid cleaning solution. A few drops of water usually collect in the lower part of the condenser tube just above the height reached by the toluene vapors. Where the amount of sample is 100 grams or more or the amount of water 10 ml. or more, the amount of these drops is too small to be considered; but to minimize it, the condenser should be cleaned frequently with hot cleaning solution.

Report.—The results shall be reported in percentage of water by weight, assuming each ml. of water to weigh 1 gram.

Precision.—The method is accurate to within 0.2 ml. of water. What this represents in percentage accuracy depends on the size of sample and amount of water. For amounts of water under 10 ml. and with accurate calibration of the trap with water under toluene, this may be increased to an accuracy of 0.1 ml.

Additional Information

1. U. S. Forest Products Laboratory Bulletin: "Chemical Analysis of Pulp and Pulp Woods," Method No. 13 (1928).
2. Schwalbe, Zeit. für Angew. Chem., **21**, 408 (1908).

METHOXYL GROUPS IN PULP[15]

Apparatus.—The apparatus shown in Fig. 271 is used for the determination of the methoxyl groups. It consists of a 50-ml. flask (*B*) connected by a ground-glass connection to a condenser the top of which forms a trap (*D*) which contains a water suspension of red phosphorous sufficient to well cover the end of the trap. At the upper end of the trap a glass tube is sealed on, leading to a series of two bubble flasks (*E*). All connections are ground glass.

A preheater (*X*) is connected to the condenser jacket, as shown, to bring the condenser to the proper temperature.

A source of dry, pure CO_2 is connected to flask *B*.

Solutions.—***Silver Nitrate.***—The $AgNO_3$ solution is prepared by dissolving 17 grams of the C.P. salt in 50 ml. of water and making it up to a liter with previously purified 95% ethyl alcohol. The aldehydes are removed from the alcohol as follows: Dissolve 1.5 grams of $AgNO_3$ in 3 ml. of water, add to 1 liter of 95% ethyl alcohol and shake well. Dissolve 3 grams of NaOH in about 15 ml. of 95% ethyl alcohol. Warm the alcohol solution gently, cool and add to the main solution. Shake the mixture well, allow to settle for several days, siphon off the clear solution and distill, adding a piece of pumice to keep the liquid from bumping.

Hydriodic Acid.—If the acid as purchased is not water-white and of sufficient sp.gr. (1.7), it must be redistilled. The acid is placed in a distillation flask and a few grams of red phosphorous added. The sides of the flask are protected from over-heating by setting the flask on a piece of asbestos which

[15] T 209 m. Tentative Standard—Feb. 16, 1932. Official Standard—April 15, 1933. Corrected—March 15, 1934. Official U. S. Forest Products Laboratory, Method No. 43, rearranged.

has a hole cut in the center sufficiently large to permit heating of only the liquid in the flask. The distillate coming over between 124–130° C. is collected and stored in a glass-stoppered brown bottle.

Test Specimen.—The specimen shall consist of about 0.5 gram of oven-dry pulp, accurately weighed.

Procedure.—The methoxyl groups are determined according to the well-known method of Zeisel. The substance to be examined is heated together with hydriodic acid, whereby methyl iodide is formed. The CH_3I is swept from the reaction flask by a current of CO_2 into vessels containing an alcoholic 0.1N $AgNO_3$ solution, the CH_3I being decomposed with the formation of AgI.

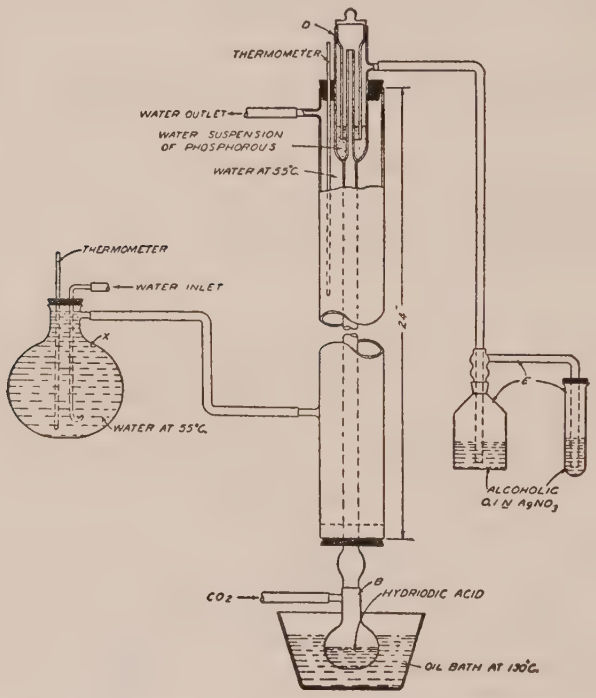


Fig. 271—.Apparatus for Determination of Methoxyl Groups.

Weigh approximately 0.5 gram of oven-dry pulp into the digestion flask (*B*), add 15 ml. of redistilled HI (sp.gr. 1.70), and heat the reaction flask in a glycerine bath at 130° C.

The temperature of the water in the condenser, used in this apparatus, is maintained at 45–55° C. by means of the preheater (*X*) through which water is kept flowing constantly by being connected to a water tap.

Absorb the CH_3I in 35 ml. of $AgNO_3$ solution placed in the absorption apparatus (*E*). Pass a current of dry CO_2 gas through the apparatus at a rate of 60 bubbles per minute. Continue heating until the $AgNO_3$ solution, at first milky, has become perfectly clear. This requires 15 minutes to 2 hours.

Wash the contents of the absorption bulb into a beaker, make up to 200 ml., add 10 ml. of conc. HNO_3 and boil the mixture gently for at least 15 minutes. After cooling this mixture filter on a tared Gooch filter. Wash the precipitate, dry for 1½ hours at 105° C., cool in a desiccator and weigh as AgI. Calculate to methoxyl, CH_3O.

Calculation: Per cent methoxyl $= 13.2 \times \frac{\text{Weight AgI}}{\text{Weight sample}}$.

Report.—The data shall be reported as a percentage of the oven-dry weight of the sample used.

Additional Information

Zeisel; Monatsh, 6, 989 (1885); 7, 406 (1886).
Manning, R. J. and Nierenstein, M., Ber. 46, 3983 (1913).
Fritz Weishut, Monatsh, 33, 1165–12 (1912).
Klemene, A., Monatsh, 34, 901–12 (1913).
Benedict and Bamberger, Monatsh, 15, 509 (1894).
Bray, M. W., Paper Trade J. 87, No. 25; 59–68 (1928).

WEIGHING, SAMPLING AND TESTING WOOD PULP FOR MOISTURE[16]

The determination of moisture in wood pulp varies with the form in which it is manufactured and the methods selected for moisture testing are specified for each given form or kind of pulp. These include: (1) baled pulp: dried sheets, shredded pulp, hydraulic pressed laps; (2) roll pulp; (3) loose lap pulp: wet laps, hydraulic pressed laps; (4) double-press wet-machine pulp in sheets.

NOTE.—Other conditions also affect the testing of pulp, such as the place, time and quantity of pulp. The place of testing may be at mill during manufacture; at dock during transfer from car to ship for export or vice versa; incoming car lots or shiploads at receiving point. The pulp may be freshly made or stored in warehouses or open piles.

Apparatus.—***Sampling Tool.***—For testing baled dry pulp, a boring tool which cuts a disk about 4 inches in diameter is used. For baled shredded pulp, a special tool (Crossley Sampling Tool made by Thompson Mfg. Co., Lancaster, N. H.) similar to a cork borer is used to cut a sample 1¼ inches in diameter and to a depth of 4 inches.

Template.—For the wedge method a template is desirable with an apex angle of approximately 4 to 9 deg. This is preferably made of brass and having a length of about 18 inches.

Laboratory Scales.—Scales used for weighing pulp samples shall show a sensibility of 0.1% of maximum load. For example, if 1 kilogram (2.2 pounds) of pulp sample is taken, the scales must show a decided deflection by the addition of 1 gram to the load.

Drying Oven.—Any suitable laboratory drying oven may be used for drying samples to constant weight. For the regulation of temperature, a thermometer shall be inserted, preferably in such a manner that the bulb when suspended in air extends as close to the center of the oven as possible. In case

[16] T 210 m–36. Official Standard—Feb., 1926. Revised—Feb. 15, 1933. Revised—April 15, 1935. Revised—Sept. 15, 1936.

a thermostatically controlled oven is used, it shall be set so as to yield a constant temperature of 215° F.±5° (102° C.±3°) and the mercury thermometer inserted as before. The thermometers used in these tests should be tested for correctness.

Test Specimen.—No one method of sampling is adequate to the many different forms of pulp. A brief mention of sampling methods and their application will be made but their fuller description will be included under the procedure to which they apply.

A. Strip Method.—The strip method, while well adapted to mill sampling of unpressed wet laps or roll pulp, is not suitable for frozen lap pulp at receiving point.

B. Boring Method.—The boring method, while well adapted to the sampling of baled pulp and rolled pulp, is not suited to the sampling of wet lap pulp, under 36% oven-dry content (40% air-dry).

C. Wedge Method.—The wedge method, or any other method which involves the breaking open of bales, is not suitable for referee sampling of pulp at dock, since transportation companies decline to handle broken bales, and rebaling with an ordinary handpress is not practicable.

D. Number of Samples.—Sufficient and representative samples from individual units must be taken to insure a fair average of the lot. This is especially necessary where grab samples from opened bales are taken.

Procedure.—***Determination of Wet Weight of Pulp.***—As all pulp is invoiced on the basis of air-dry tons, rules for the determination of the wet weight of the pulp are just as important as rules for sampling and testing, and the wet weight shall always be determined by one of the following methods:

A. Railroad Weight: Railroad weight of entire car lot where tare of empty car is actually determined by weighing it. (This does not mean the routine bill of lading railroad weight, but an actual weighing upon railroad scales supervised by a party or parties at interest.)

NOTE.—Each car shall be uncoupled from the train and weighed separately.

B. Certified Weight: Weight of entire car lot as certified by official recognized weighing bureau issuing weigh-master's certificate of weight.

C. Weighing by Truck and Tested Scales: Wet weight of lot by sum of weights of truck loads passing over accurately tested scales during loading or unloading.

D. By Calculation from Average Weight of Parcels: Wet weight of lot may also be determined by multiplying the actual number of bales or rolls in the shipment, as determined by accurate count, by the average weight of the bales or rolls weighed and sampled. When this method is used for determining the total weight, all the bales weighed, and none others, are to be sampled. In domestic roll or wet bale pulp the variation in weight between individual rolls or bales is often so great that it may be necessary to weigh the entire shipment. In the case of roll pulp or shredded pulp at least 25% of the rolls, and preferably the entire shipment, shall be weighed.

The accurate weight of all bales sampled shall be ascertained by a competent weigher before sampling; all bales weighed and no others shall be sampled (except in case of roll pulp and shredded pulp); whenever bales are numbered the number shall be given in addition to the weight.

NOTE.—Only normal bales shall be selected. A normal bale shall be intact and unbroken. Reject as abnormal those bales obviously damaged or whose weight differs from the average gross weight, as determined at the time of testing, by more than 10% plus or minus.

Scales: Scales will be accepted as accurate: (1) When verified by standard test-weights; or (2) when verified by weighing a known or measured volume of water. Scales for weighing bales shall be provided with 1 pound divisions. Those equipped with counterbalances shall not be permissible. They shall have such accuracy that they will show a variation of not more than 1 pound when a standard 400-pound weight is placed upon them after having been balanced.

Testing at Pulp Mill.—The strip method shall be used for sampling pulp coming from the wet machine or from driers in continuous web. Cut a 2 or 3-inch strip across the entire width of web coming from the machine. All strips cut shall be the same width and uniform across the machine. One sample as above described shall be taken from the wet machine for every 2000 pounds wet weight production. For web-dried pulp, one sample across the machine shall be taken for every fifth bale or roll of production.

The samples taken shall be immediately deposited in a metal can with tightly fitting cover and the net weight obtained as soon as practicable after taking samples. In case of unavoidable delay between time of taking samples and weighing, special precaution shall be taken to seal the edges of cover air-tight with friction tape or otherwise.

Weighing of Samples: Accurate laboratory scales and weights shall be used for weighing both wet and dry samples. Both wet weight and dry weight shall be obtained upon the same scales with the same weights. The hot samples shall be weighed immediately after being withdrawn from the oven in closed containers, taking care to avoid convection currents while weighing.

The entire bulk of the samples selected shall be dried out for the test. After weighing the wet samples, these shall be placed in a suitable oven and dried to constant weight at a temperature of not less than 210° F. (99° C.) and not more than 220° F. (105° C.). A minimum allowable temperature of at least 216° F. (102° C.) shall be maintained for determination of final dryness. Two successive weighings at least three hours apart shall not show a variation greater than 0.1% of the wet weight of samples and the total of the minimum weights shall be taken as the final oven-dry weight. To calculate the percentage of oven-dry pulp, divide the weight of oven-dry pulp by the wet weight and multiply by 100. To calculate the air-dry percentage, divide the percentage of oven-dry pulp by 0.9. Multiply the wet weight by this air-dry percentage and divide by 100 to obtain the weight of air-dry pulp.

Testing on Dock or Receiving Point.—The moisture determination is the same as in 2, but the sampling is different.

A. Boring Method: This is suitable for sampling (1) baled pulp in sheets, (2) roll pulp, (3) baled shredded pulp having 50% moisture or less and (4) hydraulic pressed laps having 64% moisture or less.

(1) *Baled Pulp in Sheets:*

a. Number of Bales to be Sampled: On lots of 3000 bales or less, 10% shall be taken, except by agreement, but never less than 15 bales. Samples shall be drawn from only sound and intact bales from different sections of the entire

shipment and the chemists shall be careful to observe that no unusual conditions prevail in the selection of bales.

b. Details: The samples shall be taken by boring into each bale to a depth of 3 inches, with a special tool which cuts a disk about 4 inches in diameter. Care shall be taken to see that the knife or boring tool blade does not bend when taking samples. The disks shall be removed and ten of them taken as a sample, selected as follows:

One disk from second sheet from the wrapper.
Two disks 1 inch deep.
Three disks 2 inches deep.
Four disks 3 inches deep.

The holes to be bored shall be so located that in five successive bales they will represent a portion extending diagonally across the bale. Each bale shall be bored but once, the first bale at the corner, the edges of the cut being at a distance of 1 inch from the edge of the bale. The second cut shall then be made half-way between the corner and the center of the bale; the third bale shall be cut at the center; the fourth bale halfway between the center and the corner; and the fifth bale in the opposite corner in a position corresponding to the first. In case binding wires or straps interfere with the exact location of cuts, borings shall be made as near the prescribed location as possible.

(2) *Roll Pulp:*

a. Number of Rolls to be Sampled: At least 10% of the lot, but not less than 30 rolls. Where possible to determine, the same proportion of outside rolls to center rolls should be maintained as coming from the machine.

b. Details: The edge of the first hole shall be 2 inches from one end; holes in succeeding rolls shall be spaced successively one-fifth of the distance across the roll as in bale sampling, traveling toward the opposite end of the roll. Selection of disks shall be in accordance with bale boring as given above.

NOTE.—As rolls usually vary considerably in weight, it is preferable to weigh the entire shipment or at least 25% of it.

ASH IN PULP [17]

Apparatus.—A crucible, such as platinum, alundum, or porcelain, which has a tightly fitting lid is required. It should have a capacity of 30 ml. or more.

An analytical balance sensitive to 0.1 mg.

Any suitable desiccator, such as the customary analytical desiccator which employs sulfuric acid or calcium chloride as the drying agent, may be used.

An electric muffle furnace is recommended for igniting the pulp sample. A Meker or other gas burner may be employed for this purpose.

A suitable drying oven with temperature control between 100° C. and 105° C. should also be available.

Test Specimen.—Approximately 5 grams of pulp shall be used for each determination.

[17] T 211 m–36. Tentative Standard—Feb. 15, 1933. Official Standard—March 15, 1934. Corrected—Sept. 15, 1936.

The specimen shall be representative of the lot being tested. If a carload of baled pulp is being tested, at least 10% of the bales shall be represented by small pieces composing the portion to be ashed. Reasonable modifications will necessarily be made in sampling lots of different sizes and different packing methods.

Procedure.—Ignite the empty crucible and cover over a burner, cool in a desiccator and weigh to the fourth decimal place in grams. Place the test specimen in the crucible and, after again weighing, put the whole in the drying oven, and dry the pulp to constant weight. The crucible and contents should be cooled in a desiccator and the crucible covered during weighing to prevent absorption of moisture from the air.

Place the crucible and contents in the muffle furnace (or over the burner) and ignite until all the carbon is eliminated. Heating should take place slowly at the start, and the crucible should be protected against strong drafts at all times to avoid mechanical loss. Cool the crucible in the desiccator and weigh accurately. Repeat the heating, cooling and weighing until constant weight is reached.

Calculate the percentage of ash on the oven-dry weight of the pulp and multiply this result by 0.9 to obtain the percentage on the air-dry basis.

Report.—The amount of ash shall be reported as percentage of the air-dry pulp to the nearest 0.01.

Precision.—Duplicate determinations should check within 0.03.

ONE PER CENT CAUSTIC SODA SOLUBILITY OF PULP [18]

NOTE.—For the determination of 1% caustic soda solubility of wood see T 4 m–36.

This method determines the resistance of a pulp sample to solution by hot dilute alkali. In general, the less the chemical degradation of pulp, the lower is its alkali solubility. The bulk of the material dissolved consists of pentosans and other carbohydrates which are less resistant to chemical action than cellulose, and of cellulose which has been partially broken down during the process of preparation. These are the materials which in part make up the fractions known as beta and gamma cellulose when pulp is treated in the standard manner with 17.5% NaOH solution. A cooking or bleaching treatment which is too drastic causes a chemical degradation which gives an inferior pulp, deficient in such physical properties as strength and opacity. This degradation is clearly shown by an increase in the percentage of alkali-soluble material. The test is particularly sensitive to degradation resulting from the bleaching operation and the percentage soluble will show an increase before any serious loss of physical properties is apparent. When the pulp has been overbleached enough to show a marked effect on its physical properties, the amount of soluble material will show a marked increase, often amounting to 50% of the original solubility. Thus this test is a valuable control test to detect when the cooking or bleaching processes are too drastic.

Apparatus.—The water bath employed in this determination must be so designed as to insure the temperature of the material during treatment is

[18] T 212 m–36. Tentative Standard—Feb. 15, 1933. Official Standard—March 15, 1934. Corrected—May 15, 1935. Corrected—March 27, 1936.

uniformly maintained at 97° to 100° C. When a new bath is used, the temperature of the material during the treatment should be rechecked. The type of bath recommended is one which is covered and has holes in the top large enough so that beakers may be set down into the bath until they are supported by the flared rim. The top of the beaker should be nearly level with the cover of the bath. The sides of the beaker are entirely surrounded by boiling water or steam when this type of bath is used. The height of the water in the bath should be maintained at a level above that of the liquid in the beakers.

Tall form 200-ml. Pyrex beakers should be used. Fritted glass crucibles (porosity 3) are recommended for filtering the treated pulp, although alundum crucibles of a similar porosity are also suitable.

Caustic Soda Solution.—The 1% NaOH solution (0.25 normal) is made by dissolving 10 grams of solid NaOH in water and diluting to 1 liter. Determine the NaOH content by titrating with standard acid, first using phenolphthalein as an indicator, then continuing the titration using methyl orange indicator. The difference between the volume used for the phenolphthalein end-point and that used for the methyl orange end-point represents that consumed by half the Na_2CO_3 present. By subtracting this difference from the volume used for the phenolphthalein end-point, the volume required to neutralize the NaOH is obtained, and from this volume the NaOH concentration is calculated. This shall then be adjusted to between 0.9 and 1.1%.

Test Sample.—A sample which is representative of the pulp being tested shall be air-dried and placed in an air-tight container. The moisture content shall be determined by the standard procedure. If the pulp is in the form of machine-dried or pressed sheets which do not absorb liquid readily, it should first be disintegrated to slush form in water, then filtered into pads which are dried without any pressing. In this way the pulp is obtained in a form which readily disintegrates in the alkali solution.

Procedure.—Accurately weigh on an analytical balance two samples of the air-dried pulp each equal to 2 grams of oven-dry pulp plus or minus 0.1 gram. To each sample in a tall-form 200-ml. beaker, add 100 ml. of 1% NaOH solution measured with a pipette. Stir the pulp until it is completely disintegrated, cover the beakers with watch glasses and place in the water bath, which must be boiling steadily. Leave the beakers in the bath for exactly 1 hour. Stir the contents three times, at 10, 15, and 25 minutes after being placed in the bath. At the end of the 1-hour period, filter the contents of each beaker by suction on a tared crucible. First wash the pulp briefly with hot water, then with 50 ml. of 10% acetic acid, and then wash thoroughly with hot water. Dry the crucible and contents at 105° C., cool in a desiccator, and weigh in a stoppered weighing bottle. Calculate the loss in weight of the oven-dried sample.

Report.—The results shall be reported as percentage of the oven-dry weight soluble in the NaOH solution. This value may be corrected if desired for hot-water solubility by subtracting from it the percentage of the oven-dry material soluble in hot water as determined by the standard TAPPI method (T 207 m). In this case the result shall be reported as " corrected."

Precision.—The results of duplicate tests should never vary by more than 5% of the average result, and by careful work the deviation can be kept below 2%. The results are usually somewhat higher than those obtained by the method previously used because with the old method of heating the temperature of the material during treatment was often below 90° C.

SAMPLING PAPER FOR TESTING [19]

Test Sample.—The test sample, unless otherwise specified, shall consist where possible of at least ten sheets not less than 11×11 inches in size. The sheets shall be kept smooth and flat and protected from exposure to direct sunlight and from contact with liquids and from other harmful influences. Particular care should be exercised in handling the sheets if optical tests or tests for acidity are required as such tests must be made on areas untouched by the hands.

Procedure for Sampling.—The sample sheets shall be so selected as to be as representative as possible of the entire lot of paper. Not less than 2 nor more than 5% of the total number of " units " comprising a shipment of paper shall be sampled, nor less than 5 nor more than 20 sets of sample sheets shall be taken in all. The units shall be cases, frames, or bundles, where a shipment consists of a large number of packages; or the units shall be fractions of the packages, where only a few constitute the shipment, such fractions or units comprising not less than 1,000 sheets each.

Sets of sample sheets from sheet-cut paper shall each consist of 10 consecutive sheets; except for lots containing fewer than 10 units, when each set shall consist of 5 consecutive sheets; provided that if there are reasons to believe that the paper was cut and stacked in single or any definite number of sheets together, each sample set shall also consist of that number. The sheets shall be taken from a point or points over ½ inch from the top or bottom of each frame, case or bundle.

From rolls a single sheet shall be taken across the first unharmed layer; except when the shipment comprises less than 5 rolls, when the sheets may be taken across the first two unharmed layers.

The sample sheets shall be trimmed with their edges exactly parallel to the machine and cross directions of the paper.

The sample sheets comprising each set shall be consecutively numbered and sufficient specimen sheets bearing consecutive numbers shall be taken for testing purposes, one from each set in rotation.

Procedure for Resampling.—In case of necessity for resampling a lot of paper, the samples shall be taken as described above except that they shall, if possible, be drawn from units different from those previously sampled.

[19] T 400 m–36. Official Standard—July, 1926. Revised—Nov. 22, 1934. Revised —Sept. 15, 1935. Corrected—Sept. 15, 1936.

CONDITIONING PAPER FOR TESTING[20]

NOTE.—This method is the official standard of the Technical Association. Many laboratories, however test at different temperatures and humidities. This is allowable, provided the conditions employed are stated in the report. Unless such a statement is made it will be assumed that the conditions stated in the official standard prevail.

Relative Humidity and Temperature.—Whenever required in a test method, the paper sample shall be conditioned and tested in an atmosphere maintained at 65% relative humidity and 21° C. (70° F.) temperature. A tolerance is permissible (unless for very precise work) of plus or minus 2 in the percentage relative humidity (63 to 67%) and of plus or minus 3° C. (5.5° F.) in temperature.

Conditioning.—Each test specimen of the paper sample shall be so suspended that the conditioning atmosphere will have free access to all surfaces. Means shall be provided for so circulating the air of the conditioning and testing chamber that its humidity and temperature will be uniformly maintained. The conditioning time shall be sufficient for the moisture content of the specimen to attain equilibrium with the conditioning atmosphere, this to be determined by conditioning to constant weight, by very accurate weighings at intervals of not less than one-half hour.

For work of such precision that the hysteresis in the equilibrium moisture content may lead to an appreciable error, the moisture content equilibrium under standard conditions shall be approached from a drier state by first reducing, if necessary, the moisture content to less than half the value under standard conditions and then conditioning under standard conditions. For that purpose the samples may be dried in a desiccator or other convenient means, provided the temperature does not exceed 60° C. (140° F.).

NOTE.—With good circulation a conditioning period of 4 hours is usually sufficient for papers of ordinary weight and composition, but some hard-sized papers, boards and water-resistant specialties may require 24 hours or longer.

Determination of Humidity and Temperature.—The relative humidity of the conditioning atmosphere shall be determined by means of either (1) a sling psychrometer, or (2) a stationary type of psychrometer having the air circulated over the thermometer bulbs mechanically. In both cases the circulation of air round the thermometer bulbs shall be at the rate of not less than 3 meters (10 feet) per second and the exposure not less than 60 seconds before the readings are taken. When the sling type is used, care shall be taken to make the readings, especially of the wet bulb, as quickly as possible after bringing it to rest. For a relative humidity of 65% with temperature about 70° F., at 30 inches atmospheric pressure, the wet bulb should be depressed 7.7° F. from the dry bulb reading.

The thermometers used for determining humidity and temperature shall be accurately calibrated by comparison with certified standard thermometers and any corrections found necessary applied to the readings.

NOTE.—It is recommended that thermometers approaching the following specifications be used: Range 0–50° C. (32–122° F.); graduation, 0.2° C. (0.5° F.). They should

[20] T 402 m–36. Official Standard—July, 1926. Revised—Nov. 22, 1934. Corrected—Sept. 15, 1936.

be matched to within ¼° F. throughout the range used. Under ordinary conditions an error of 1 in the percentage relative humidity corresponds to an error of approximately ¼° F. in the wet bulb depression. Except for high altitudes, the barometric correction is negligible.

PARAFFIN IN PAPER [21]

Apparatus.—An extraction apparatus with a reflux condenser is necessary for this test. The balance used for weighing shall be sensitive to 0.1 mg.

Test Specimen.—The test specimen shall consist of not less than 5 grams of air-dry paper obtained by cutting small strips from different portions of the test sample in such a way as to be representative of it. The strips shall be cut into small pieces about 6 mm. (0.25 inches) square. It is recommended that the test specimen be ground or shredded.

Procedure.—Completely extract the paraffin from the paper with chemically pure carbon tetrachloride, in the extraction apparatus. Evaporate the extract to dryness, add 25 ml. of 0.5 N alcoholic potash, and again evaporate to dryness. Take up the dry residue with ether and water, and transfer to a separatory funnel. The volume of ether in the funnel should be 25 ml. and that of the water, 150 ml. The water should contain a small amount of sodium chloride to prevent emulsification. Shake the contents of the flask thoroughly, allow separation to take place, and draw off the water into a second separatory funnel. Repeat the treatment, one or more times as may be found necessary, with a fresh 25-ml. portion of ether. Combine the ether extracts, and wash with fresh 100-ml. portions of water until the separated liquids are perfectly clear. An addition of a strong solution of sodium chloride to the ether extract may be necessary to thoroughly clarify it. Transfer the ether extract to a weighed evaporating dish, evaporate to dryness, dry for exactly one hour at 100° C. and weigh the dried residue to an accuracy of 0.1 mg. Not less than two determinations shall be made and the average of the results shall be computed. The percentage results of duplicate determinations of paraffin shall agree within 0.2.

Report.—The paraffin content shall be expressed as a percentage of the air-dry paper to the nearest 0.1.

ACTIVE SULFUR IN PAPER [22]

Apparatus.—The special apparatus required for this determination consists of a 500-ml. round-bottomed distillation flask having a neck about 5 cm. (2 inches) long and 25 cm. (1 inch) in diameter, and a tube 10 cm. (4 inches) long so connected to the mouth of the flask that all gases generated in the flask will pass through a filter paper clamped between the mouth of the flask and the end of the tube, and then out through the tube.

The balance used for weighing shall be sensitive to 1 mg. or less.

Test Specimen.—The specimen shall consist of 0.250 gram of air-dry paper, either ground or thoroughly disintegrated by shaking in water.

[21] T 405 m-36. Official Standard—July, 1926. Revised—Jan., 1930. Corrected—Sept. 15, 1936.

[22] T 406 m-36. Official Standard—July, 1926. Corrected—Sept. 15, 1936.

Reagents.—(*a*) Copper sulfate solution made by dissolving 0.786 gram of C.P. crystals of $CuSO_4 \cdot 5H_2O$ in water and diluting to 1 liter. 10 ml. of this solution contain 0.002 gram of Cu.

(*b*) Small pieces of C.P. stick zinc, free from sulfur and arsenic, activated as follows: Cover the zinc with the $CuSO_4$ solution, using 10 ml. for each gram of Zn. After allowing to stand a few minutes for deposition of the Cu, wash the Zn with water until free from $ZnSO_4$. The Zn can be reactivated several times.

(*c*) Concentrated C.P. hydrochloric or phosphoric acid, free from S and As.

(*d*) C.P. lead acetate, 10% solution.

(*e*) C.P. sodium thiosulfate, 0.001% solution.

(*f*) Sulfur-free surgical absorbent cotton prepared by boiling in a dilute solution of NaOH and washing thoroughly with water.

Procedure.—Transfer the weighed specimen to the distillation flask with 20 ml. of distilled water and add approximately 2 grams of activated Zn cut in small pieces, and 10 ml. of conc. HCl or H_3PO_4. Insert in the neck of the flask a loose wad of surgical absorbent cotton about 4 cm. (1½ inches) long. Clamp between the mouth of the flask and the tube a hardened filter paper (such as Schleicher and Schülls' No. 575) which has been freshly moistened with 10% Pb-acetate solution. Place another wad of absorbent cotton in the tube above the filter paper. Prepare flasks under duplicate conditions, containing in place of the paper under test, pure, sulfur-free cotton, and measured amounts of Na-thiosulfate solution. Set all the flasks in a steam bath for 1 hour, frequently agitating the contents. Remove the filter papers and allow them to air-dry. Determine the percentage of sulfur present by comparing the depth of the color developed by the S from the specimen with that developed by the known amounts of S evolved from the thiosulfate solutions.

As 0.000001 gram of S will give a distinct stain, care must be taken to protect the paper under test from contamination. It must be protected from atmospheric fumes and should not be handled with the bare hands.

Report.—The amount of sulfur shall be reported as a percentage of the air-dry paper.

NOTE.—In respect to the tarnishing effect of sulfur, a paper containing not more than 0.0008% of S is required for wrapping silverware.

Additional Information

Sutermeister, E.: "Chemistry of Pulp and Paper Making," p. 422, John Wiley, New York.

AMOUNT OF COATING OF MINERAL COATED PAPER[23]

This method is suitable for the ordinary types of mineral coatings. It may not be effective for exceptional special types, such as where lacquers or other materials are used to impart a high degree of water resistance.

Reagent.—***Enzyme Solution.***—Aqueous solution of approximately 1.5 grams of enzyme and 25 ml. of 0.1 N NaOH per liter.

The enzyme recommended by Sutermeister and Porter (1) is trypsin, but

[23] T 407 m. Official Standard—July, 1926. Tentative Revision—Jan. 15, 1934. Revised—April 15, 1935.

some of the mixtures of enzymes used commercially for desizing cotton and degumming silk have been found to be more rapid in action, less expensive, and more stable. The preparation Degoma D. L. made by Röhm & Haas Co., 222 West Washington Square, Philadelphia, Pa., is particularly suitable.

Test Specimen.—The specimen for test shall consist of not less than 25 square inches.

Procedure.—Obtain the air-dry weight of the specimen. Place it in a suitable container in such a way that the enzyme solution will have free access to the entire surface of the coating. It may be laid in a flat-bottomed tray or rolled in cylindrical form and placed in a burette. Pour over the specimen sufficient enzyme solution to cover it completely. Allow to stand for at least 1 hour at 50° C., then place the paper on a pane of glass and brush off the coating with a camel's hair brush, taking care not to dislodge the paper fibers. Additional heating, and in some cases additional enzyme solution, may be found necessary for very resistant coatings.

After the coating is entirely removed, stand the glass pane at a slight angle and wash the paper on both sides by means of a wash bottle, holding the paper on the glass by one corner. Dry the specimen and obtain the air-dry weight. The difference between this weight and the original weight of the specimen is the amount of coating material. Not less than two determinations shall be made and the average of the results shall be reported.

Report.—The amount of mineral coating shall be reported (1) as a percentage of the decoated air-dry paper and (2) as pounds per 500 sheets, 25×40 inches in size. The weight of the decoated air-dry paper, on this same weight basis, shall also be included in the report.

Precision.—Owing to the variable nature of coating materials, the precision is variable. With most ordinary types of coatings, the percentage of coating material found should be correct to within 0.5 to 2.

Literature Cited

1. Sutermeister and Porter, Tech. Assoc. Papers, XIII, No. 1; 205 (1930).

RESIN IN PAPER[24]

Apparatus.—A suitable extraction apparatus, such as the Soxhlet or the Underwriters', is required for this determination. In addition, if glue or other nitrogenous sizing agents are present, two 300-ml. separatory funnels are necessary.

Reagent.—***Acidulated Alcohol.***—To 190 ml. of 95% alcohol add 1 ml. of glacial acetic acid and 19 ml. of water, and mix.

Test Specimen.—The test specimen shall consist of not less than 5 grams of paper obtained by cutting strips approximately ½ inch wide from the sample in such a way as to be representative of it. It is recommended that the specimens be shredded or ground.

Procedure.—Obtain the air-dry weight of the specimen. If the paper is not shredded or ground, fold the strips into numerous crosswise folds and place

[24] T 408 m-36. Tentative Standard—Feb. 27, 1917. Official Standard—July, 1926. Corrected—Sept. 15, 1936.

them in the siphon cup of the extractor. Extract with acidulated alcohol, siphoning at least 12 times or as many more as may be necessary until the solvent siphons over colorless.

If nitrogenous sizing agents are present, they must be separated from the resin as follows, this not being necessary in absence of such materials. Wash the alcoholic extract of resin, which may contain foreign material, into a beaker and evaporate to a few ml. on a steam bath. Cool, take up in about 25 ml. of ether, transfer to a 300-ml. separatory funnel containing about 150 ml. of water to which has been added a small quantity of sodium chloride to prevent emulsification, shake thoroughly and allow to separate. Draw off the water into a second separatory funnel and repeat the treatment with a fresh 25-ml. portion of ether. Combine the ether extracts which contain the resin and any other ether-soluble material, and wash twice, or until the ether layer is perfectly clear and the line between the ether and the water is sharp and distinct, with 100-ml. portions of water to remove salts and foreign matter. Should any glue, which may be extracted from the paper, interfere by emulsifying with the ether, it may be readily removed by adding a strong solution of sodium chloride to the combined ether extracts. Shake thoroughly and draw off the aqueous solution, repeating if necessary before washing with water.

Transfer the alcoholic or the ether extract to a weighed evaporating dish, evaporate to dryness, dry the residue exactly 1 hour at 100° C., and weigh to an accuracy of 0.1 mg. Not less than two determinations shall be made, and the average of the results computed. The percentage results of duplicate determinations of resin should agree within 0.2.

Report.—The resin content shall be expressed as a percentage of the air-dry paper, to the nearest 0.1 per cent.

Additional Information

"Quantitative Determination of Rosin in Paper."—C. F. Sammet, Ind. & Eng. Chem., 5, 732 (1913); Paper 13, No. 1, 17 (1913).

NOTE.—See also T 416 m, Rosin in Paper (Qualitative).

MOISTURE IN PAPER[25]

Apparatus.—The special apparatus required for this determination is an air-tight container in which the specimen is dried and weighed. For the minimum size specimen designated, a weighing bottle approximately 65 mm. (2.56 inches) in height and 45 mm. (1.77 inches) in diameter is suitable. For larger specimens, proportionately larger containers should be used.

The oven used to dry the paper shall be equipped with means for ensuring adequate temperature control and air circulation and preferably equipped with means of drying the air entering the oven.

Test Specimen.—The specimen for test shall consist of not less than 2 grams of paper obtained by cutting small strips from different portions of the test sample in such a way as to be representative of it.

NOTE.—When the paper under test is not in moisture equilibrium with the surrounding atmosphere, take care to minimize the time of exposure of the test sample to the atmosphere as much as possible, gain or loss of moisture being very rapid under this condition.

[25] T 412 m. Official Standard—Dec., 1926. Corrected—May 15, 1935.

Procedure.—Place the specimen in a weighed air-tight container, close the container and obtain the weight of the specimen. Remove the cover of the container and dry the paper in the container, in an oven having an adequate circulation of air, at 100–105° C. (212–221° F.), for one hour. Close the container in the oven, remove to a desiccator and cool in the desiccator to room temperature. Weigh the container and paper and repeat the entire process until the weight is constant. All weighings shall be made to an accuracy of 1 mg. The percentage results of duplicate determinations of moisture shall agree within 0.2.

Report.—Report the amount of moisture as a percentage, (1) of the original weight of the paper and (2) of the oven-dry paper, to the nearest 0.1.

ASH IN PAPER[26]

Apparatus.—A crucible, such as platinum, alundum or porcelain, which will not change in weight under the ignition conditions used and with a tightly fitting lid; a balance sensitive to 1 mg.; and a desiccator, are necessary for this determination. An electric muffle furnace is recommended for burning the paper.

Test Specimen.—The test specimen shall consist of not less than 1 gram of air-dry paper obtained by cutting small strips from different portions of the sample in such a way as to be representative of it.

Procedure.—Weigh the specimen of paper accurately in the previously weighed crucible and ignite completely. To avoid loss of small particles of the specimen care must be taken to heat it slowly and to protect the contents of the crucible at all times from strong drafts. When the paper is completely burned, as indicated by absence of black particles, remove the crucible to the desiccator, cover and allow to remain until its temperature has reached equilibrium with that of the surrounding atmosphere. Then weigh the crucible and contents and repeat the ignition and weighing until the weight is constant.

All weighings shall be made to an accuracy of 1 mg.

Precision.—The percentage results of duplicate determinations shall agree within 0.2.

Report.—The amount of ash shall be reported as a percentage of the air-dry paper to the nearest 0.1.

Additional Information

See T 211 m Ash in Pulp.

PROTEINACEOUS NITROGEN IN PAPER[27]

Apparatus.—A Kjeldahl digestion and distillation apparatus is required for this determination. A 500-ml. Kjeldahl flask is a suitable size.

Test Specimen.—The specimen shall consist of from 3 to 5 grams of air-dry paper, obtained by cutting small strips from different portions of the test sample in such a way as to be representative of it. The strips shall be cut into pieces approximately 6 mm. (0.25 inch) square.

[26] T 413 m. Official Standard—Dec., 1926. Corrected—April 15, 1935.
[27] T 418 m. Official Standard—Dec., 1926. Corrected—May 15, 1935

Procedure.—*Gunning Method.*—Place the specimen, weighed to an accuracy of 1 mg., in the Kjeldahl flask and add 10 grams of powdered anhydrous sodium sulfate, a small crystal of copper sulfate (about 0.2 gram) and 25 ml. of conc. sulfuric acid. Heat the flask gently until frothing has ceased and then digest with increasing temperature until oxidation is complete, i.e., for a short time after the mixture becomes clear and colorless, or nearly so. Cool and dilute with about 200 ml. of water. Add about 2 ml. of liquid petrolatum to prevent foaming and about 2 grams of 30-mesh granulated zinc to prevent bumping during the distillation. Add a saturated solution of NaOH to the contents of the flask in such amount (usually 75 ml.) that there is an excess of 5 ml. present. This solution must be poured carefully down the side of the flask so that it does not mix with the acid contents. The total volume of the solution should be about 400 ml.

Immediately connect the flask to a condenser having its delivery tube just beneath the surface of a known amount of 0.1 N sulfuric acid diluted to 100 ml. (30 ml. of 0.1 N acid is usually sufficient). Mix the contents of the Kjeldahl flask by shaking the flask, then heat it gradually and distill the contents for about 45 minutes, taking care to avoid spurting. The total volume of the distillate should be about 200 ml.

Titrate the contents of the receiver flask with 0.1 N alkali, using methyl red indicator. The difference between the number of ml. of 0.1 N alkali used and the ml. of 0.1 N acid added to the receiver flask is the number of ml. of 0.1 N acid equivalent to the nitrogen present. This number multiplied by 0.0014 is the nitrogen found.

The percentage results of duplicate determinations of nitrogen shall agree within 0.02. A blank determination shall be made on all reagents used and any nitrogen found subtracted.

Report.—The amount of N shall be expressed as a percentage of the air-dry paper to the nearest 0.01%. If it is desired to report the percentage of glue or casein present, it shall be calculated by multiplying the percentage of N found by 5.6 and 6.3 respectively.

NOTE.—As these factors vary with different kinds and grades of material, they should be determined whenever the nitrogenous material is available, and whenever possible the N in the paper before addition of the nitrogenous material should be determined and subtracted from the total N found.

STARCH IN PAPER[28]

QUALITATIVE

NOTE.—This was formerly printed as a separate method T 419 m.

A positive result obtained by the following method shall be regarded as conclusive evidence of the presence of starch in paper.

Boil about 0.5 gram of paper for several minutes with 10 ml. of water. Filter off the extract, cool it, and add one drop of approximately 0.001N iodine solution. A blue coloration indicates starch. If only a faint violet

[28] T 419–420 m. Official Standard—Dec., 1926. Revised—January, 1930 Corrected—March 15, 1934.

coloration is obtained, this should be disregarded, as non-starch constituents of paper sometimes give such reaction.

NOTE.—It is convenient to make an approximately 0.01 N stock solution of iodine (0.13 gram I and 2.6 grams KI in 100 ml. water) and dilute a portion of this to a pale yellow color (about 0.001 N) each time a test for starch is made.

QUANTITATIVE

NOTE.—This was formerly printed as a separate method T 420 m.

Apparatus.—A reflux condenser is necessary for this test. The balance used for weighing shall be sensitive to 1 mg.

Reagents.—***For Use of Fehling's Solution.***—(*a*) Copper sulfate (Fehling's Solution A)—To 4 liters of distilled water add 277.3 grams of crystallized copper sulfate ($CuSO_4$, $5H_2O$), and shake the mixture at intervals until the crystals have dissolved. The $CuSO_4$ should be of high purity and as free from Fe as possible.

(*b*) Alkaline Tartrate (Fehling's Solution B)—Dissolve 150 grams of sodium hydroxide of good quality and 500 grams of potassium sodium tartrate in 1500 ml. of distilled water.

(*c*) Mixed Fehling's Solution—Prepare by careful addition of the copper sulfate solution A to an equal volume of the alkaline tartrate solution B. It may be kept ready mixed but should in this case be carefully protected from light and air. It is, however, preferable to keep the solutions separate until they are needed.

(*d*) Molybdophosphoric Solution—Dissolve 100 grams of sodium molybdate (43% Mo) and 75 ml. of syrupy phosphoric acid (85%) in a solution containing 275 ml. of conc. sulfuric acid and 1750 ml. of distilled water.

(*e*) Potassium Permanganate Solution—Prepare a N/30 solution of $KMnO_4$ by dissolving 1.10 grams in distilled water and making up to 1 liter. Standardize against sodium oxalate.

For Use of Benedict's Solution.—The directions for preparing this solution are described by Joslin (Diabetic Manual Paper 197) as follows:

Copper sulfate (C.P. crystals)	14.20 grams
Anhydrous sodium carbonate	100 grams
Sodium citrate ($5\frac{1}{2}$ H_2O)	200 grams
Potassium sulfocyanate	125 grams
5% potassium ferrocyanide solution	10 ml.
Distilled water to make a volume of	1000 ml.

With the aid of heat dissolve the carbonate, citrate and sulfocyanate in enough water to make about 800 ml. of the mixture. Dissolve the $CuSO_4$ (accurately weighed) separately in about 100 ml. of water and pour the solution into the other liquid with constant stirring. Add the ferrocyanide solution, cool and dilute to exactly 1 liter. Only the copper sulfate need be weighed with exactness.

Test Specimen.—The specimen shall consist of not less than 5 grams of oven-dry paper obtained by cutting small strips from different portions of the test sample in such a way as to be representative of it. The strips shall be cut into small pieces about 6 mm. (0.25 inch) square.

Procedure.—Place the weighed specimen of paper in a 500-ml. round-bottomed flask, add 200 ml. of water and 5 ml. of glacial acetic acid. Connect the flask to a reflux condenser and boil the contents vigorously for 1.5 hours. Pour the contents of the flask through a Büchner funnel and wash the pulp on the plate with 50 ml. of hot water, using suction. Add 15 ml. of conc. HCl to the filtrate and boil under reflux for 30 minutes. Neutralize the hot solution with solid Na_2CO_3 until effervescence ceases. Cool to room temperature and adjust to 500 ml. in a volumetric flask. Determine the starch in the hydrolized starch solution with either Fehling's solution or Benedict's solution. The procedure for each of these solutions follows:

1. *With Fehling's Solution:* Draw off 100 ml. of this hydrolized starch solution by means of a pipette into a 400-ml. beaker. Add 25 ml. of mixed Fehling's solution and boil for 10–15 minutes. Filter through a small Büchner funnel containing an asbestos mat. Wash the cuprous oxide with 200 ml. of hot water. Transfer the Cu_2O with the asbestos mat back to the original beaker and add 25 ml. of the molybdophosphoric solution. Add 25 ml. of water and filter off the asbestos through the same Büchner funnel. Wash the mat with 200 ml. of cold water, removing every trace of blue color. Titrate the filtrate with N/30 $KMnO_4$ solution to a faint pink after the blue color has been discharged.

1 ml. N/30 $KMnO_4$ = 0.0011 gram starch.

2. *With Benedict's Solution:* To approximately 10 grams of Na_2CO_3 in a 150-ml. beaker, add 20 ml. of water and 5 ml. of Benedict's solution. Heat to boiling and add the hydrolized starch solution from a burette in small portions. Keep the solution in the beaker boiling and maintain its volume at about 25 ml. The end-point is when the Benedict's solution changes to colorless.

1 ml. Benedict's solution = 0.002 gram starch.

As the factor for starch varies with different kinds and grades, when the starch used in the paper is available its exact factor can be determined by the following procedure:

Dry the starch at 100–105° C. for 3 hours. Weigh exactly 0.05 gram and boil with approximately 190 ml. of 4% HCl solution for 30 minutes. Neutralize with Na_2CO_3, cool, adjust to a definite volume, and titrate against either of the solutions as described. When it is desired to express the content of starch on an air-dry basis and the actual initial moisture content of the starch is not known, the average moisture figure of 12% may be used in the conversion calculation.

Report.—The amount of starch shall be reported as a percentage of the oven-dry paper to the nearest 0.01%.

Additional Information

This method is based on that of V. Voorhees and O. Kamm.[29] The original method was revised in respect to the Fehling solution (suggested by Miss H. U. Kiely) and the Benedict solution (suggested by G. P. Genberg), to avoid use of indicators and to obtain a sharper end-point.

[29] Paper, 24; 1091 (Aug. 27, 1919).

MINERAL FILLER IN PAPER[30]

Test Specimen.—The specimen for test shall consist of not less than 0.2 gram of ash obtained from the paper by the official method for determining the ash of paper (T 413 m).

Procedure for Qualitative Determination.—Warm the ash in a small quantity of dil. HCl. An effervescence indicates the presence of carbonate. If there is an insoluble residue, decant the acid solution through a filter paper and repeat the operation twice, finally transferring the residue to the filter paper and washing it thoroughly.

Add an excess of NH_4OH to a portion of the acid solution. A white, gelatinous precipitate shows the presence of Al. Filter off any such precipitate and add a solution of NH_4-oxalate. A white granular precipitate indicates Ca. To another portion of the acid solution add a few drops of $BaCl_2$ solution and warm. A white precipitate will form if a sulfate compound is present.

Dry any residue from the acid treatment of the ash, burn off the filter paper in a platinum crucible, and add to the contents of the crucible a fusion mixture consisting of equal parts of Na and K carbonates. Fuse to a clear mass, cool, transfer the fusion to a beaker and heat gently with water. When the mass is thoroughly disintegrated, filter and wash any residue thoroughly with hot water. To the filtrate add an excess of HCl, evaporate to dryness, and treat the residue with warm dil. HCl. A white, transparent, flaky precipitate shows the presence of silica. Filter off such precipitate and to half of the filtrate add a solution of $BaCl_2$, when a white precipitate will form if an insoluble sulfate, such as $BaSO_4$, was present in the paper. To the other half of the filtrate add an excess of NH_4OH and boil. A white gelatinous precipitate indicates Al_2O_3.

Dissolve the water-insoluble portion of the fusion with dil. HCl. Add to the solution an excess of NH_4OH and boil. A white gelatinous precipitate shows the presence of Al. Filter off any such precipitate and add NH_4-carbonate to the filtrate. A white precipitate occurs if Ba is present. Filter and add an excess of ammonium phosphate and stir thoroughly after cooling. A white crystalline precipitate indicates Mg.

A considerable amount of Ca and sulfate in the ash soluble in HCl indicates the presence of calcium sulfate, $CaSO_4 \cdot 2H_2O$ (crown filler). The presence of Ba and sulfate in the acid-insoluble portion of the ash indicates $BaSO_4$ (blanc fixe or barytes). An alkaline ash containing Ca soluble in HCl but with no sulfate present indicates the presence of $CaCO_3$ (whiting or chalk). The presence of Ba in ash which is soluble in HCl with effervescence indicates $BaCO_3$. Considerable amounts of silica and Al indicate aluminum silicate added as china clay. Considerable amounts of silica and Mg indicate magnesium silicate derived from talc or asbestine. A microscopical examination of the ash assists in determining the variety of silicious minerals present.

Procedure for Quantitative Determination.—The procedure for determining the amounts of the various fillers present follows that given for their qualitative determination. The methods used for ensuring quantitative separation and determination of the various constituents are those described in

[30] T 422 m. Official Standard—Sept., 1927. Corrected—May 15, 1935.

standard textbooks dealing with mineral analysis. When the ashing of the paper causes chemical changes in the filler, the actual amount of filler originally present must be calculated. The more common examples of such changes are: loss of combined water in clay and crown filler; loss of CO_2 in carbonates; reduction of sulfates to sulfides.

Additional Information

Griffin, R. C., "Technical Methods of Analysis." McGraw-Hill, New York.

TOTAL ACIDITY OF PAPER [31]

Apparatus.—The special apparatus required for this test is a grinder which will completely disintegrate the paper without heating or contaminating it and a steam or oil bath which can be maintained at 100° C. The grinder shall be a "Dr. Koerner" type or its equivalent.

The balance used for weighing shall be sensitive to 1 mg.

The glassware shall be acid- and alkali-resistant.

Reagents.—(*a*) 0.01 N sodium hydroxide solution, conveniently made by diluting 100 ml. of 0.1 N NaOH to 1 liter with freshly boiled and cooled distilled water.

(*b*) Phenolphthalein indicator solution.

Test Specimen.—The specimen for test shall be cut from the test sample in such a way as to be thoroughly representative of it, and shall be completely disintegrated in the grinder.

Procedure.—Allow the ground specimen to come to moisture equilibrium with the atmosphere of the balance case, and weigh 5-gram portions (to nearest 1 mg.) for the acid extractions and moisture determination at the same time. Determine the moisture content on one portion by the standard TAPPI method. Transfer another weighed portion to a 500-ml. Erlenmeyer flask and add 250 ml. of boiling water. In some cases, the fibers absorb water slowly and tend to float on the surface of the water. This is avoided by first adding small portions of the water and shaking well until the fibers are thoroughly saturated. After the water is added, affix to the flask a stopper containing a narrow glass tube about 30 inches in length, which serves as a condenser. A soil-digestion flask which has a ground-glass stopper and condensing tube in one piece, or a rubber stopper covered with metal foil, may be used. Place the flask in a heating bath which will maintain the contents of the flask at 95° to 100° C. Heat at this temperature for one hour with occasional shaking. At the end of this period pour the contents of the flask on a Büchner funnel (without other filtering medium) and wash the fibers remaining in the flask into the Büchner funnel with 10 ml. of water. Apply strong suction to the fibers, then return them to the flask. Cool the extract rapidly and titrate as soon as it reaches room temperature, with 0.01 N NaOH, using phenolphthalein indicator. Make two additional extractions and titrations exactly as in

[31] T 428 m-36. Tentative Standard—March, 1932. Corrected—Sept. 15, 1936. This method has been approved by the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry. Suggestions and criticisms should be sent to R. G. Macdonald, 122 East 42nd Street, New York, N. Y.

the first instance. Make a blank titration on 250 ml. of the water heated for 1 hour in the same bath and with the same glassware used for the extractions. Each test result used in calculating the acidity shall be the average of not less than two determinations. The results of duplicate determinations of total acidity shall agree within 0.01.

Report.—Total acidity shall be expressed as a percentage of the moisture-free paper in terms of sulfuric anhydride, SO_3, to the nearest 0.01. It is calculated as follows:

Let T = ml. NaOH required to neutralize the 3 extracts;
t = 3 times the ml. NaOH required to neutralize the blank;
N = normality of the NaOH solution; and
W = weight of test specimen less moisture.

Then, $$\frac{(T-t)\times N\times 0.04\times 100}{W} = \text{per cent } SO_3.$$

Additional Information

This method is that described by S. Kohler and G. Hall in The Paper Industry, **7**, No. 7; (Oct. 1925), with some modifications developed at the U. S. Bureau of Standards.

Studies of this method and other acidity methods are reported by Wehmhoff and by Wehmer in Technical Association Papers (TAPPI), May, 1930 and May, 1931.

The Dr. Koerner type of grinder is described in U. S. Bureau of Standards Research Paper No. 295.

ALPHA CELLULOSE IN PAPER[32]

NOTE.—See also T 203 m-36.

This method is for papers free from unbleached, ground-wood, or other highly lignified fibers, such as the ordinary types of writing and printing papers used for record purposes.

Apparatus.—The special apparatus required for this test is:

A grinder which will completely disintegrate the paper without heating or contaminating it. The grinder shall be a "Dr. Koerner" type or its equivalent.

A water bath which can be maintained at 20° C.

A 7.5-cm. Büchner funnel with a nainsook cloth filter cut to fit the funnel, the cloth having been previously washed to remove stiffening material, and dried against glass. Dry the cloth to constant weight at 105° C. and weigh it in a weighing bottle before using it.

The balance used for weighing shall be sensitive to 1 mg.

The glassware used shall be of acid- and alkali-resistant grade.

Reagents.—***Sodium Hydroxide Solution.***—Dissolve pure NaOH in an equal weight of water and allow the solution to stand in a stoppered glass vessel until it becomes clear. Filter the supernatant solution through an asbestos mat and dilute it with water free from CO_2 to a sp.gr. of 1.197 at 15° C. The

[32] T 429 m-36. Tentative Standard—March, 1932. Corrected—Sept. 15, 1936. This method has been approved by the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry. Suggestions and criticisms should be sent to R. G. Macdonald, 122 East 42nd Street, New York, N. Y.

solution will then contain 17.5% of NaOH by weight. This should be checked by titration and should be adjusted if necessary within the limits 17.4–17.6.

Acetic Acid.—Approximately a 20% solution in water.

Test Specimen.—The specimen for test shall be cut from the test sample in such a way as to be thoroughly representative of it, and shall be completely disintegrated in the grinder.

Procedure.—Allow the specimen to come to moisture equilibrium with the atmosphere of the balance. Weigh (to the nearest 1 mg.) approximately 5 grams of the disintegrated paper. Weigh at the same time samples for moisture and ash determinations, and for determinations of such other non-cellulose components as may be found necessary for correction of the alpha cellulose figures (total resins, starch, glue, etc.). These determinations shall be made by the TAPPI standard methods. When mineral filler is present, the weight of it shall be calculated from the ash content. The weight of mineral coating shall be determined likewise, or according to the standard TAPPI method.

Transfer the specimens for alpha cellulose determination to a 400-ml. beaker, adjust the beaker and contents in a water bath at 20° C., add 50 ml. of the NaOH solution accurately measured with a pipette, and note the time immediately after this is added. Macerate the mixture thoroughly with a flattened glass rod, and add a second 50-ml. portion of the NaOH solution, this addition being made after about 5 minutes have elapsed from the time of the first addition. Macerate the mixture again and let it stand with occasional stirring for a total time of 30 minutes from the time of first addition of NaOH. At the end of this period, dilute the mixture with 250 ml. of distilled water having a temperature of 20° C. and filter it immediately with gentle suction, using a 7.5-cm. Büchner funnel with a nainsook cloth filter cut to fit the funnel, the cloth having been previously washed to remove stiffening material, and dried against glass. Dry the cloth to constant weight at 105° C. and weigh it in a weighing bottle before using it. Wash as uniformly as possible with 125 ml. of water at exactly 20° C. and then return the filtrate to the funnel and allow it to pass through the pad. Then wash the pad with 750 ml. of water having a temperature of exactly 20° C. Occasional packing of the pad with the flattened glass rod is necessary during the washing as the pad has a tendency to shrink and permit the wash water to flow around its edge and not through it. Follow the water with 100 ml. of 20% acetic acid at about 20° C. and let the pad stand in this condition for 5 minutes, without application of suction. Finally apply suction and wash the pad with 1 liter of water at about 95° C.

Transfer the pad and cloth to a Petri dish or watch glass, dry at 70° C. for 3 hours, transfer to a weighing bottle, dry to constant weight at 105° C. and weigh in the closed weighing bottle. Determinations shall be made of ash and other non-cellulosic components of the residue as may be found necessary, so that the weight of the residue may be corrected for these components.

The weight of the residue, after deduction of non-cellulosic constituents, divided by the weight of the test specimen, likewise corrected, and the result multiplied by 100, gives the percentage of alpha cellulose in the total cellulosic content. The weight of the test specimen shall always be corrected for moisture and both the test specimen and the residue shall always be corrected

for ash. Both the test specimen and the residue shall be corrected for other non-cellulosic components whenever they are present in significant amounts. Not less than two determinations shall be made and the average of the results shall be reported. Duplicate determinations shall agree within 0.3.

Report.—The amount of alpha cellulose shall be reported as percentage of the total cellulosic content to the first decimal place.

Additional Information

Cross and Bevan [33] mention the use of NaOH of mercerizing strength in isolating "normal" cellulose. The method described here is based on that of Jentgen [34] and modification of his method suggested by Parsons [35] and Ross [36] and by Burton and Rasch.[37]

COPPER NUMBER OF PAPER [38]

Apparatus.—This method is for papers free from unbleached, ground-wood, or other highly lignified fibers, such as the ordinary types of writing and printing papers used for record purposes.

The special apparatus required for this test is (1) a grinder which will completely disintegrate the paper without heating or contaminating it and (2) a steam or oil bath which can be maintained at 100° C. The grinder shall be a "Dr. Koerner" type or its equivalent.

The balance used for weighing shall be sensitive to 1 mg.

The glassware used shall be acid- and alkali-resistant.

Reagents.—***Copper Sulfate Solution.***—Dissolve 100 grams of copper sulfate ($CuSO_4 \cdot 5H_2O$) in water and dilute to 1 liter.

Carbonate-Bicarbonate Solution.—Dissolve 350 grams of sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) and 50 grams of sodium bicarbonate ($NaHCO_3$) in water and dilute to 1 liter.

Molybdophosphoric Acid.—Dissolve 100 grams of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and 75 ml. of phosphoric acid (83%) in a mixture of 275 ml. of concentrated sulfuric acid and 1.75 liters of water.

Sodium Carbonate Solution.—An approximately 5% solution of Na_2CO_3 in water.

Potassium Permanganate Solution.—0.05 N.

Test Specimen.—The specimen for test shall be cut from the test sample in such a way as to be thoroughly representative of it, and shall be completely disintegrated in the grinder.

Procedure.—Allow the specimen to come to moisture equilibrium with the atmosphere of the balance. Weigh about 1.5 grams (to nearest 1 mg.) of the

[33] Cross and Bevan, "Researches of Cellulose," Vol. III, 1905–1910, p. 22.

[34] Jentgen, *Kunstoffe*, **1**, 165 (1911).

[35] Parsons, *Paper Trade Journal*, **82**, No. 8, p. 211 (Technical Section, p. 105).

[36] Ross, "Research Notes" (Canadian Pulp and Paper Association, Vol. 1, p. 105), 1926.

[37] Burton and Rasch, Bureau of Standards *Jour. of Research*, R. P. No. 295, April, 1931. Includes an illustrated description of the "Dr. Koerner" grinder.

[38] T 430 m-36. Tentative Standard—March, 1932. Corrected—Sept. 15, 1936. This method has been approved by the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry. Suggestions and criticisms should be sent to R. G. Macdonald, 122 East 42nd Street, New York, N. Y.

ground paper. Weigh at the same time, samples for moisture and ash determinations, and for determinations of such other non-cellulose components (total resins, starch, glue, etc.) as may be found necessary for correction of the copper number. These determinations shall be made by the TAPPI standard methods. When mineral filler is present, the weight of it shall be calculated from the ash content. The weight of mineral coating shall be determined likewise, or according to the Tappi standard method.

Immediately before use add 5.0 ml. of solution A to 95 ml. of B. Bring the mixture to a boil in 2 minutes, and pour it over 1.5 grams of the finely ground sample in a 125-ml. Erlenmeyer flask. Stir well with a glass rod in order to distribute the fibers and to remove air bubbles. Fit the flask with a loosely fitting glass bulb or stopper and submerge completely in a steam bath at atmospheric pressure. Occasionally fibers tend to float to the surface, therefore the flask should be shaken from time to time to redistribute them. Remove the flask from the steam bath at the end of 3 hours. Filter on an ashless filter paper in a 7.5-cm. Büchner funnel, using suction. Wash by flooding with 100 ml. of 5% Na_2CO_3 solution at about 20° C. and then by flooding with 250 ml. of hot water (about 95° C.). Transfer the fibers and filter paper to a small beaker, add 25 ml. of the molybdate solution and macerate well with a flattened glass rod. Transfer to a Büchner funnel again and wash thoroughly with cold water until the blue molybdenum color is removed from the fibers. Dilute the filtrate with water to approximately 700 ml. and titrate it with 0.05 N $KMnO_4$ to a faint pink.

The copper number is defined as the number of grams of metallic copper in the cuprous oxide reduced from the cupric hydroxide by 100 grams of the paper fibers. This is calculated as follows:

$$\text{Copper Number} = \frac{6.357 \times \text{ml. } KMnO_4 \times N}{W},$$

where N is the normality of the $KMnO_4$ and W is the weight in grams of the test specimen after deduction of the weight of the non-cellulosic materials. Correction of the weight of the test specimen shall always be made for moisture and ash. Correction for other non-cellulosic components shall be made whenever they are present in significant amounts. Not less than two determinations shall be made and the average of the results shall be reported. Duplicate determinations shall agree within 0.1.

Report.—The copper number shall be reported on the basis of the total cellulosic content to two decimal places.

Additional Information

This method is essentially the Braidy [39] modification of the original Schwalbe [40] method, with modifications for its adaption to paper proposed by Scribner and Brode,[41] and by Burton and Rasch.[42]

[39] A thorough investigation of the Braidy method was made by Clibbens and Geake, (J. Text. Inst., **15**, T 31, 1924).

[40] Die Chemie der Cellulose, p. 625; 1912.

[41] Technologic Paper No. 354, National Bureau of Standards.

[42] Bureau of Standards Jour. of Research, R. P. 295, April, 1934. Includes an illustrated description of the "Dr. Koerner" type of grinder.

ACID-SOLUBLE IRON IN PAPER[43]

The procedure commonly used for this purpose is to extract the ash of the paper with acid but investigation has shown that the procedure described below is preferable because: (1) it requires less time; (2) in the ashing of the paper, some of the soluble iron may be volatilized and some of the insoluble iron may be made soluble. The removal of the acid-soluble iron is complete. This is considered the portion of the iron present that is potentially chemically reactive, as distinguished from insoluble or " fixed " iron such as might occur as silicate or other complex compound in clay filler.

Reagents.—***Ammonium Sulfocyanate Solution.***—Dissolve approximately 76 grams of pure NH_4SCN in water and dilute to 1 liter.

Standard Iron Solution.—Dissolve 14.04 grams of pure ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, and 4.07 grams of pure ammonium persulfate, $(NH_4)_2S_2O_8$, in water containing 1 ml. of conc. H_2SO_4. Mix well and dilute to exactly 1 liter. Dilute 25 ml. of this solution to 1 liter. When 5 grams of paper are used, 1 ml. of this standard equals 10 parts of Fe per million parts of paper.

Test Specimen.—The specimen for test shall be cut from the sample in such a way as to be thoroughly representative of it and shall be either cut in small squares (about ¼-inch) or ground. Cutting the paper in small pieces is generally sufficient, but grinding of very hard, resistant paper may be found necessary.

Procedure.—Drench 5 grams of paper with 50 ml. of concentrated HCl. Cold acid usually suffices but hot acid may be required if large particles of iron are present. After the paper is thoroughly saturated with the acid, filter on a 7.5-cm. Büchner funnel. Wash the residue with three 50-ml. portions of hot water, applying suction after each addition. Add a few drops of concentrated HNO_3 to the combined filtrates, make ammoniacal with concentrated NH_4OH, and boil until the odor of NH_3 is nearly but not quite gone. Filter through a filter paper and wash the residue on the paper thoroughly with hot water. Place the funnel containing the filter paper and $Fe(OH)_3$ in the neck of a 50-ml. volumetric flask, and add two successive 5-ml. portions of dil. HCl (1 : 3), with intermediate and final washing with water. Dilute the filtrate to 150 ml. Measure 10 cc. of this solution into a 50-ml. Nessler tube and add enough 0.05 N (or 0.1 N) $KMnO_4$ solution to completely oxidize the iron, or until there is a faint pink color to the solution. Add 10 ml. of the NH_4SCN solution, dilute to the mark, mix, and compare immediately with standards made in the same way with the standard iron solution.

The standard iron comparates shall be prepared freshly for each comparison, as they fade rapidly. A blank determination on the reagents shall be run and a correction applied if necessary. At least two determinations shall be made and the average of the results shall be reported. Duplicate determinations should agree within 5 parts per million.

Report.—The results shall be reported as parts of acid-soluble iron per million parts of paper by weight.

[43] T 434 m. Tentative Standard—Jan. 15, 1934. Official Standard—April 15, 1935.

Additional Information

American Public Health Association, "Standard Methods of Water Analysis," 1933. (The modified procedure for paper was suggested in a communication from A. E. Kimberly, Bureau of Standards.)

HYDROGEN ION CONCENTRATION (pH) OF PAPER EXTRACTS [44]

Apparatus.—***Grinder.***—The grinder shall be capable of completely disintegrating the paper without heating or contaminating it. The type described by Burton and Rasch (1), and known as the Koerner type, is recommended.

Glassware.—The glassware used shall be resistant to acids and alkalies. Pyrex glass or its equivalent is recommended.

Colorimetric and Electrometric pH Apparatus.—Any of the usual forms of colorimetric apparatus employing indicators and glass comparison tubes is suitable. The apparatus recommended for the electrometric determination is illustrated in Fig. 272. In addition to this there is required a potentiometer and galvanometer similar to the Leeds and Northrup student or precision

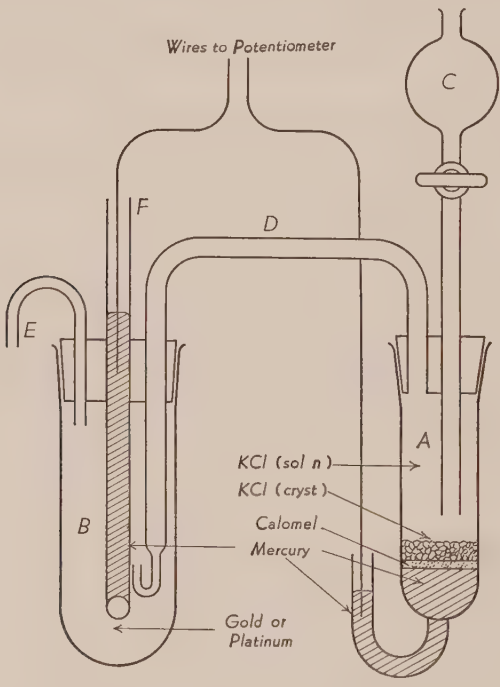


Fig. 272.—Electrometric pH Apparatus.

[44] T 435 m. Tentative Standard—Sept. 6, 1934. This method has been approved by the Paper Testing Committee as a tentative standard. Send comments to R. G. Macdonald, 122 E. 42nd Street, New York, N. Y.

instruments, for measuring the voltage. In the figure, *A* is a saturated calomel electrode. A platinum wire sealed through the bottom serves to connect the mercury in the tube electrically with that in the outside arm. The electrode is prepared by placing pure mercury in the tube to a depth of about 1 cm., covering this with a 2-mm. layer of calomel (preferably electrolytically prepared), adding pure KCl crystals to a depth of about 1 cm., and filling the tube with a solution of KCl saturated at the temperature at which the electrode is to be used. The funnel *C* serves as a reservoir for this solution. *B* is a wide-mouthed test-tube which contains the solution under examination. It is fitted with a stopper bearing a glass tube *D* which connects this vessel with the calomel electrode. The lower end of *D* is drawn out as a capillary and bent up as shown, and the entire tube is filled with saturated KCl solution from *C*. The stopper also contains a narrow glass tube *E*, which serves as an air vent, and an electrode *F*. The electrode illustrated may be used as a quinhydrone electrode. In such case, the solution being tested is saturated with quinhydrone by adding approximately 0.5 gram of the solid of as high purity as possible and stirring.

This electrode is the simplest one to use and is satisfactory if the pH of the extract is less than 8, and if the buffer concentration of the extract is not too small. If the pH is greater than 8, some other electrode must be used, such as the hydrogen or antimony electrode. These electrodes, however, do not function well at low buffer concentrations and are " poisoned " by certain materials which may be present in the extract. The most universally useful electrode is the glass electrode which can be used through the entire range of pH up to about pH 11 and which is not sensitive to " poisons." The use of the glass electrode, however, requires an especially sensitive galvanometer (3) (4) (5). It is recommended that the glass electrode be used wherever the equipment is available. In all cases the apparatus used is the same except the electrode *F*, which must be selected to suit the type of extract being tested.

Test Specimen.—The test specimen shall be cut from the test sample in such a way as to be thoroughly representative of it. It shall be completely disintegrated in the grinder.

Procedure.—***Extraction.***—Weigh 5 grams of air-dry paper to the nearest 0.1 gram. For the extraction, transfer the specimen to a 500-ml. flask and add 250 ml. of boiling distilled water. The water should be of high purity, preferably double or triple distilled. The quality of the water is particularly important in the determination of the pH of papers having low acidity, such as unsized papers. In such cases the water should have a pH between 6.6 and 7.0. If the fibers tend to float on the surface of the water, add water in small portions, stir until the fibers are thoroughly wetted, then add the remainder of the water. After the water is added, affix to the flask a stopper containing a glass tube about 8 to 10 mm. in diameter and 75 cm. in length, which serves as a condenser. A soil-digestion flask which has a ground-glass stopper and condensing tube in one piece, or a rubber stopper covered with clean metal foil, may be used. Place the flask in a heating bath which will maintain the contents of the flask at 95° to 100° C. without boiling the water. Heat at this temperature for 1 hour with occasional shaking. Pour the contents of the flask on a Büchner funnel without other filtering medium, and

draw the solution through the fiber mat with strong suction. Disconnect the suction just before the filtration is completed. As a few fibers may go through the funnel with the first portion of solution, return the filtrate to the flask and again pass it through the mat. Pour the filtrate into a clean flask, close it tightly with a clean rubber stopper, and set aside to cool to room temperature. The extract must be protected from the air as much as possible at all times to avoid CO_2 contamination.

pH Measurement.—(*a*) *Colorimetric*: In using the colorimetric method care must be taken that the indicators are adjusted in pH, either at the midpoint of their range, or at frequent intervals (e.g. 0.2 pH) throughout their usual range for more accurate work. This is necessary because paper extracts are usually not well buffered, and the addition of an indicator may change the pH of the extract sufficiently to cause an appreciable error unless the pH of the indicator is near that of the extract. The Acree-Fawcett isohydric indicator method (6) (7) is recommended. This procedure consists of locating the approximate pH of the unknown solution by testing with an indicator solution adjusted at the midpoint of its range and then making a further precision determination with indicator solution adjusted at the approximate pH. This may be most easily accomplished by using solutions of indicator adjusted at intervals of 0.2 pH throughout the effective range of the indicator. The adjustment is made by comparing the color of 0.001 M indicator solution with 0.05 M buffer-color standards while adding to it 0.01 N HCl or NaOH as required to match the color standard having the desired pH. Following is the suggested procedure:

(1) Add 0.2 ml. of midpoint indicator to 10 ml. of extract in a test tube.

(2) Compare with 0.05 M buffer color standards and obtain the approximate pH.

(3) Repeat (1) by using indicator solution adjusted at the approximate pH value obtained in (2).

(4) Compare the color standards and read to nearest 0.1 pH.

This method is simple and convenient, and checks the electrometric method very closely within the limits of its accuracy. The average of the results of at least two determinations shall be reported. The results should agree within 0.2 pH.

(*b*) *Electrometric:* Referring to Fig. 272, flush the tube *D* by opening the stopcock on *C* momentarily with *B* removed. Fill the vessel *B* with the extract to the depth indicated and fit it to the stopper as shown. Run a small amount (about 0.1 ml.) of the saturated KCl solution out through the capillary opening in *D*. Connect the wires from *A* and *F* to a potentiometer and measure the voltage. Take readings until the voltage is constant to about 1 millivolt for a period of several minutes. Calculate the pH from the voltage readings, *E*, by the following equations:

$$\text{pH} = \frac{0.4526 - E}{0.0591} \text{ for the quinhydrone electrode.}$$

$$\text{pH} = \frac{E - 0.2358}{0.0591} \text{ for the hydrogen electrode.}$$

The voltage obtained with the antimony or glass electrode depends upon the individual electrodes used. The pH can be calculated from the voltage by calibrating the electrodes against buffers of known pH. In some cases these calibrations are furnished by the manufacturers of the electrodes. The above equations are for a temperature of 25° C. but they may be used for measurements made at ordinary room temperature within the degree of accuracy stated below, by changing the denominator plus or minus 1/298 of its value, respectively, for each ° C. above or below 25. These equations are valid only when the saturated calomel electrode is used as the reference electrode.

The average of the results of at least two determinations shall be reported. The results should agree within 0.1 pH.

Report.—Results shall be reported as the pH of the air-dry paper. They shall be rounded off for the colorimetric method to the nearest 0.1, and for the electrometric method to the nearest 0.05. The report shall state which of these methods was used.

Literature Cited

For an illustrated description of a grinder suitable for disintegrating the paper see:
1. Burton and Rasch, U. S. Bur. of Standards Jour. of Research, **6**, 605 (Research Paper 295) (1931).

For detailed description of suitable electrometric methods see:
2. Clark, W. M.: "The Determination of Hydrogen Ions," Williams and Wilkens Co., Baltimore (1928).
3. Burton, Matheson and Acree, U. S. Bur. of Standards Jour. of Research, **12**, 67 (Research Paper 436) (1934).
4. Leeds and Northrup Company, Philadelphia, Pa.
5. American Instrument Company, Washington, D. C.

For a description of a suitable colorimetric method see:
6. Fawcett and Acree, Jour. of Bacteriology, **17**, 171 (1926).
7. Fawcett and Acree, Ind. Eng. Chem., Anal. Edition, **2**, 78 (1930).
8. "Modern pH and Chlorine Control," Bulletin of W. A. Taylor and Company, Baltimore, Md.

A study of certain of the details of this method is reported in the following articles:
9. Wehmhoff, B. L.: "The Determination of the pH Values and Total Acidity of Paper," Tech. Assoc. Papers, **13**, p. 231, May, 1930; **14**, p. 387, May, 1931.

ARSENIC IN PAPER [45]

Apparatus.—The modified Gutzeit apparatus for determination of arsenic is shown in Fig. 273.

Two sizes of the apparatus are desirable; No. 1 for use when the paper contains less than 0.01 mg. of arsenic trioxide (As_2O_3) and No. 2 for use where the paper contains more than that amount. The dimensions of apparatus No. 1 are listed to the left of the sketch; those of apparatus No. 2 are listed to the right.

Reagents.—***Concentrated Nitric Acid,*** arsenic-free, having a sp.gr. of at least 1.4.

Concentrated Sulfuric Acid, arsenic-free, having a sp.gr. of at least 1.8.

Zinc, arsenic-free, in the form of sticks (Bureau of Standards Standard

[45] T 436 m–36. Tentative Standard—May 15, 1935. Official Standard—Sept. 15, 1936.

Sample No. 43C is recommended). Break the sticks into pieces about 1 cm. long, rinse with water and treat with HCl until the surface of the Zn is clean. Then wash with water, dry and store in a clean, wide-mouthed, glass-stoppered bottle.

Mixed Acid.—Dilute 1 volume of As-free H_2SO_4 with 4 volumes of water, and to this add 10 grams of NaCl for each 100 ml. of solution.

Ferric Ammonium Alum Solution.—Dissolve 84 grams of the salt, $Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$, in water, add 10 ml. of the mixed acid and dilute to 1 liter.

Lead Acetate Solution (for wetting glass wool).—Add to a 5% solution of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, sufficient acetic acid to clarify the solution.

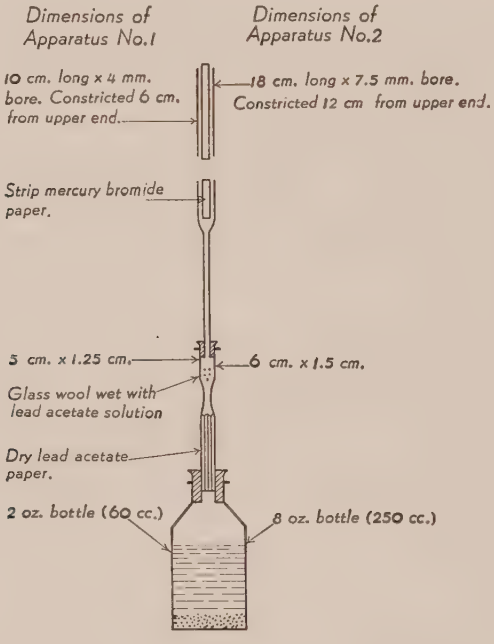

Dimensions of Apparatus No.1
Dimensions of Apparatus No.2
10 cm. long x 4 mm. bore. Constricted 6 cm. from upper end.
18 cm. long x 7.5 mm. bore. Constricted 12 cm from upper end.
Strip mercury bromide paper.
5 cm. x 1.25 cm.
6 cm. x 1.5 cm.
Glass wool wet with lead acetate solution
Dry lead acetate paper.
2 oz. bottle (60 cc.)
8 oz. bottle (250 cc.)

Fig. 273.—Gutzeit Apparatus (modified).

Stannous Chloride Solution.—Dissolve 80 grams of $SnCl_2$ in 100 ml. of water containing 5 ml. of As-free, concentrated HCl.

Lead Acetate Test Paper (for removal of H_2S).—Soak large sheets of filter paper, qualitative grade, in a 5% solution of Pb-acetate, dry, and cut into pieces 7×5 cm. for apparatus No. 1 and 11×9 cm. for apparatus No. 2.

Mercuric Bromide Paper.—Dry several pieces of Whatman No. 40 filter paper at 100–105° C. for 1 hour and store in a desiccator over fused $CaCl_2$. Cut the paper into strips 2.5 mm. wide and saturate with a 1.5% solution of $HgBr_2$ in 95% ethyl alcohol. Dry in a desiccator for 10 minutes and use promptly. No treated strips should be stored longer than 2 hours before use.

Standard Arsenic Solution.—Dissolve 1.000 gram of resublimed arsenious oxide (As_2O_3) in 25 ml. of 20% As-free NaOH solution and neutralize with dil. H_2SO_4, using methyl orange indicator. Dilute this solution to 1 liter with freshly distilled water, to which 10 ml. of concentrated H_2SO_4 have been added for each liter of solution. Mix well and again dilute 10 ml. of the solution to 1 liter with water containing H_2SO_4. Finally, dilute 100 ml. of the latter solution to 1 liter with water containing acid. One ml. of the final solution contains 0.001 mg. (or 1 microgram) of As_2O_3.

Standard Stains.—Prepare 2 sets of stains by running blank determinations to which are added definite amounts of the standard As solution, the determinations being conducted exactly as described below under Procedure.

The first set of stains should be those made by 0.001, 0.002, 0.004, 0.006, 0.008, 0.010, 0.015 and 0.020 mg. of As_2O_3, respectively. This set is convenient for use with apparatus No. 1 and covers the range of As content of most papers. The second set of stains should be those made by 0.02, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 mg. of As_2O_3, respectively. This set of stains is convenient for use with the apparatus No. 2 and for larger samples of paper.

Preservation of Stains.—Dip the sensitized paper containing the As stain, as soon as prepared, in molten paraffin, free from water, and mount on a sheet of white paper, folded back to form a cylinder. The white paper cylinder should be dried in an oven at 105° C. before mounting the standard stains. It is important that the standard stains and the white paper cylinder be kept dry, or the stains will soon fade. Place the cylinder with the stains mounted on it in a glass test tube containing phosphorous pentoxide covered with glass wool, close the glass tube with a rubber stopper and store the tube in a dark place.

Test Specimen.—Cut 5 grams [46] of the air-dry paper under test (weighed to the nearest mg., if arsenic is to be reported as parts by weight, or measured accurately (±0.1 in.) for area if arsenic is to be reported as parts per unit area) into pieces from ⅛ to ¼ inch square, and place in a porcelain casserole. Add 10–15 ml. of concentrated HNO_3 and cover the casserole by setting a watch glass inside the rim, convex side up, with a thin glass rod between the wall of the casserole and the edge of the watch glass. (This eliminates removing the watch glass for the addition of acids during digestion of the paper.) Heat on a hot-water bath until vigorous action ceases. Cool and add 10 ml. of concentrated H_2SO_4. When vigorous action ceases, heat gently on the water bath until the mixture liquefies and is dark brown or black in color. Then alternately cool, add concentrated HNO_3 in 5-ml. portions, and heat on the hot plate between additions of HNO_3 until the solution remains colorless to yellow when evaporated to the evolution of white fumes of SO_3. To completely remove all nitric or nitrous acid, evaporate to about 10 ml., cool, dilute with 10–15 ml. of water and again evaporate to fumes of SO_3. Cool, dilute with water, cool again, and make up to 100 ml. with water in a volumetric flask.

For a blank correction on the acids used, place in a separate casserole the total quantity of acids used to digest and oxidize the paper sample, and heat until all nitric and nitrous acids are driven off and white fumes of SO_3 are evolved. Cool and make up to 100 ml. in a volumetric flask.

[46] This amount is suitable for most papers but may have to be varied in special cases.

Procedure.—Place 5 or 6 strips of Pb-acetate paper in the lower tube of the absorption tower, a loose wad of glass wool moistened with Pb-acetate solution in the upper tube, and a strip of $HgBr_2$ paper in the topmost tube of the absorption tower of the Gutzeit apparatus. Then pipette 20 ml. of the prepared solution of the test specimen into the flask of the apparatus, add 2 ml. of ferric ammonium alum solution, 0.5 ml. of $SnCl_2$ solution, 50 ml. of mixed acid and sufficient water (in this case 27.5 ml.) to make a total volume of 100 ml. Add 8–10 grams of Zn to the solution in the flask, immediately connect the absorption tower and set the flask in a water bath maintained at about 20° C. Let the evolution of gas continue for 1 hour, then remove the test strip of bromide paper, dip it into molten paraffin and place it in a test tube such as used for storing the standard stains. Prepare a stain from the blank solution in the same manner as used for the solution of the paper test-specimen. Compare both stains with the set of standards, and assign to each "unknown" stain the value of the standard stain which most nearly matches it in color. Deduct the value of the blank stain from that obtained from the solution of the paper test-specimen. The difference is the amount of As, calculated as As_2O_3, in the solution tested. Multiply by 5 to obtain the amount of As_2O_3 in the paper specimen used.

Report.—The results shall be reported as either: (a) parts of arsenic trioxide per million parts of paper, or (b) grains of metallic arsenic per square yard of paper.

Calculations:

Let W = weight in grams of specimen tested;
S = area in square inches of specimen tested; and
A = value in mg. of As_2O_3 of matching stain (corrected for blank and for aliquot of solution used).

Then

(a) $\frac{1000A}{W}$ = parts As_2O_3 per million parts of paper, and

(b) $\frac{15.15A}{S}$ = grains of arsenic per square yard of paper.

Additional Information

"Standard Methods of Chemical Analysis," 5th Ed., Vol. I, pp. 101–108.
Griffin, R. C., "Technical Methods of Analysis," 2nd Ed., pp. 52 and 56. McGraw-Hill, New York, N. Y. (1927).
Hillebrand & Lundell, "Applied Inorganic Analysis," pp. 218–220. Wiley & Sons, New York, N. Y. (1929).
Official Methods of The Association of Official Agricultural Chemists, 3d Ed., p. 306. Williams & Wilkins, Baltimore, Md. (1930).

ZINC PIGMENTS IN PAPER[47]

The zinc pigments used as paper fillers comprise three main classes: (1) zinc sulfide alone, (2) high-strength zinc pigment, containing about 50% ZnS and 50% $BaSO_4$, and (3) low-strength zinc pigment, containing less than 30% ZnS

[47] T 438 m–36. Tentative Standard—Aug. 1, 1936.

(the balance $BaSO_4$), typified by lithopone. These pigments may be used alone or in combination with other fillers, such as clay, etc.

Reagents.—*Dilute HCl (5 : 9).*—To 5 volumes of concentrated HCl add 9 volumes of water. This solution contains about 15% of HCl or 157 grams per liter.

0.3% HCl.—Dilute 10 ml. of the above solution with 500 ml. of water.

Dilute H_2SO_4 (1 : 1).—To 1 volume of water add 1 volume of concentrated H_2SO_4.

Ammonium Chloride Solution.—To 500 ml. of water add 25 ml. of concentrated NH_4OH and 10 ml. of concentrated HCl.

Potassium Ferricyanide Solution.—Dissolve 1 gram of $K_3Fe(CN)_6$ in 100 ml. of water.

Diphenylamine Indicator.—To 100 ml. of concentrated H_2SO_4 add 1 gram of diphenylamine.

Standard Potassium Ferrocyanide Solution.—To 1 liter of water add 6.46 grams of $K_4Fe(CN)_6 \cdot 3H_2O$. One ml. of this solution should be equivalent to 0.0015 gram of Zn. Standardize by titrating a solution of known Zn content as described under Procedure. If it is desired to calculate the results of Zn determination on the paper in terms of one of the three main types of Zn pigment listed above, the solution should be standardized against that type of pigment. In this case dissolve a weighed amount of the pigment in the diluted HCl, boil to remove H_2S, adjust the acidity of the solution to between 0.5 and 1.0 normal, add 2 drops of diphenylamine indicator and titrate with the standard ferrocyanide solution. If the pigments used contain Fe or Al, which is unusual, these must be removed before titration, as they interfere. If merely the Zn equivalent of the standard solution is desired, a solution of chemically pure zinc should be used. (Bureau of Standards Sample 43 is recommended.)

Test Specimen.—The test specimen shall be large enough to contain at least 10 mg. of Zn (0.8 g. is usually sufficient), obtained by cutting pieces about ¼ inch square from the sample in such a way as to be thoroughly representative of it. The oven-dry weight of the specimen shall be determined according to TAPPI Standard Method T 412 m.

Procedure.—Place the weighed specimen in a 150-ml. beaker, add 20 ml. of water and 8 ml. of the dilute HCl, cover the beaker with a watch glass and boil gently for about 10 minutes. Wash down the sides of the beaker and also the watch glass with 0.3% HCl. Pour the liquid through a filter (Whatman No. 4 or 41 or S & S 589—black ribbon) into a 600-ml. beaker, keeping as much of the pulp in the beaker as possible. Press the pulp against the side of the beaker with a glass rod to remove most of the solution. Wash the pulp twice with 0.3% HCl, each time squeezing the pulp as before, and wash the filter twice with more of the same acid (see note 1). Add 2 ml. of dilute H_2SO_4 to the filtrate and boil. Keep the beaker covered with a watch glass. Add concentrated HNO_3, a few drops at a time, until all organic matter is destroyed. Then boil the solution, keeping the watch glass on until most of the solution is evaporated; then remove the cover and heat on the hot plate until copious white fumes of SO_3 appear and all HNO_3 has been removed, especially any condensed on the sides of the beaker.

Cool the solution to approximately room temperature and dilute with 500 ml. of water. Heat to boiling and make distinctly alkaline with concentrated NH_4OH. (About 5 ml. are usually sufficient.) Filter the solution through S & S No. 589 black ribbon filter paper (or Whatman No. 4 or 41) and wash the precipitate well with NH_4Cl solution. About 4 washings are usually sufficient (see note 2). Boil the filtrate until free from NH_3 odor, concentrate by evaporation to 50–75 ml., add 5 ml. of concentrated HCl, 2 drops of ferricyanide solution, 2 drops of diphenylamine indicator solution, and titrate with the standard ferrocyanide solution to the disappearance of the purple color (see note 3). The volume of standard ferrocyanide solution used, multiplied by its Zn equivalent, gives the amount of zinc in the sample.

Report.—The amount of zinc (or the appropriate zinc filler, if known) shall be reported as a percentage of the oven-dry paper to the nearest 0.1.

NOTES.—1. When filtering the pulp from the solution after boiling, and in the subsequent washing, the pulp should be pressed as dry as possible. This requires some skill and becomes quite difficult with weak, short-fibered pulps. In such cases it may be better to use a Gooch crucible or a Büchner funnel fitted with a filter paper.

2. Where the paper tested contains considerable clay, the initial boiling with HCl may be shortened slightly. This keeps the solution of Fe and Al at a minimum. If a voluminous precipitate of $Al(OH)_3$ is obtained when the NH_4OH is added, it is very difficult to wash the precipitate free from Zn. In this case it is best to dissolve the precipitate in HCl and reprecipitate with NH_4OH, combining the two filtrates. Two solutions and reprecipitations, with a final washing with NH_4Cl solution, will remove all Zn from the Fe and Al hydroxides.

3. The volume of the solution to be titrated should be between 50 and 75 ml. The indicator is somewhat sensitive to acidity and salt concentration, but satisfactory results will be obtained if the solution is prepared as directed. Excessive amounts of NH_4-salts, especially when only small amounts of Zn are present, may render the end-point somewhat indistinct. Therefore, if resolution and reprecipitation have been resorted to because of large Fe and Al precipitates, care should be taken to keep the NH_4OH and HCl used as small as possible.

The solution should be stirred actively during the titration, and when only a small amount of Zn is present, the standard ferrocyanide solution should be added very slowly. In some cases it requires some time for the color to develop after addition of the first portions of the ferrocyanide. A false end-point usually occurs, where the blue color changes to purple, which sometimes takes a few seconds to appear. After this point the ferrocyanide is added drop by drop until the purple color disappears and does not return after stirring the solution for 20 seconds. This color change at the end-point is ordinarily sharp and distinct, if there are more than 10 mg. of Zn present.

Additional Information

Zinc and titanium pigments are sometimes found together in paper fillers. Ti does not interfere with the determination of Zn as detailed above.

When one of the three main classes of Zn pigments listed above occurs alone in a paper and the ash of the pulp is known, the zinc pigment can be determined by direct ignition, taking care to maintain a plentiful supply of air during combustion, to prevent possible reduction of the Zn salt to metallic Zn with subsequent volatilization, thereby giving low results. Only 0.5 to 1 gram of the paper should be used; the crucible containing it should be placed in the very dull red portion of the furnace and most of the carbon burned off. The residual carbon can be burned off at 800–850° C. with the furnace door ajar and no cover on the crucible.

The weight of the ash, corrected for the ash of the pulp, if this is known, should be multiplied by a factor which takes into account the loss in weight due to conversion of ZnS to ZnO on ignition. The usual factors for the three main types of zinc pigments are as follows:

(1) ZnS—1.19
(2) "High-Strength" zinc pigment—1.09
(3) "Low-Strength" zinc pigment —1.06

References

Kolthoff and Pearson, "Titration of Zinc with Potassium Ferrocyanide," Ind. Eng. Chem., Anal. Ed. **4**, 147 (1932).
Steele, F. A., "The Determination of Zinc Sulfide Pigments in Paper," Paper Trade J., **97**, No. 9, 27 (1933).

TITANIUM PIGMENTS IN PAPER [48]

This method deals with the analysis of paper ash as modified by the presence of titanium pigments, i.e. (1) pure titanium dioxide, (2) titanium dioxide-barium sulfate composite, and (3) titanium dioxide-calcium sulfate composite.

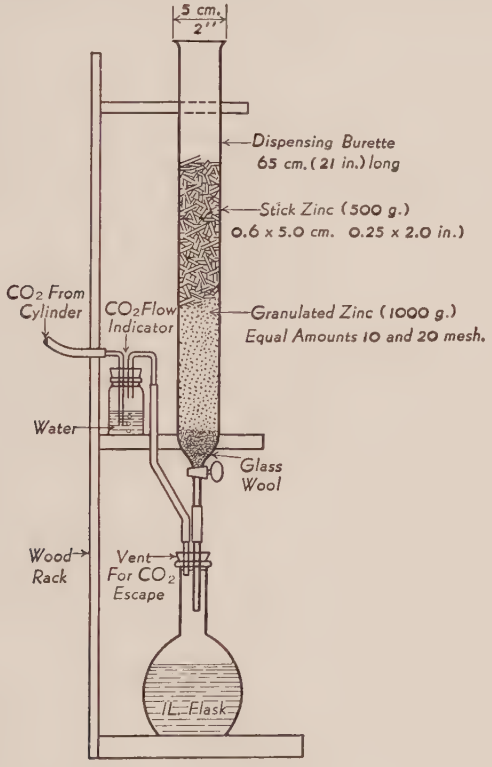


FIG. 274.

Apparatus.—The only special apparatus required is a Jones reductor, shown in Fig. 274. This consists of a glass tube about 2 inches in diameter and 21

[48] T 439 m-36. Tentative Standard—Aug. 1, 1936.

inches long with a glass stopcock at the bottom. (An ungraduated dispensing burette is satisfactory.) It is connected to a liter flask as shown in the figure. A means is also provided for introducing CO_2 into the flask through a bubble trap. The tube is filled for about one-third of its length with 1000 grams of a mixture of equal amounts of 10-mesh and 20-mesh granulated zinc resting on a pad of glass wool. The upper portion of the tube contains 500 grams of stick Zn in pieces about 2 inches long. Before use the Zn is amalgamated as follows: Place 250 grams of the Zn in a heavy glass flask, add a solution of 11 grams of mercuric chloride in 100 ml. of concentrated HCl, swirl the mixture for a few minutes, pour off the liquid, and wash the Zn free from acid with water.

NOTE.—When not in use the Jones reductor should be kept filled with water and covered to exclude dust and other extraneous matter.

Reagents.—***0.1 N Potassium Permanganate Solution,*** standardized against U. S. Bureau of Standards sodium oxalate.

Standard Ferric Alum Solution, of which 1 ml. is equivalent to about 0.005 gram of TiO_2; standardized by reduction and titration with 0.1 N $KMnO_4$.

Dissolve 30 grams of $Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$ in 300 ml. of water acidified with 10 ml. of H_2SO_4 and add $KMnO_4$ solution drop by drop as long as the pink color disappears. Finally dilute the solution to 1 liter. To standardize, dilute 50 ml. of the solution, measured from a burette, to about 100 ml. with dilute H_2SO_4 (1 : 20), reduce in the Jones reductor and titrate against the 0.1 N $KMnO_4$.

Thiocyanate Indicator.—A saturated solution of NH_4SCN.

Test Specimen.—Sufficient paper shall be ashed according to TAPPI standard T 413 m to yield the required amount of ash. The oven-dry weight of the paper shall be determined according to TAPPI standard T 412 m.

Procedure.—***Qualitative.***—A qualitative analysis of the ash should be made, unless the nature of the loading material is known, since it will greatly facilitate the quantitative analysis. The procedures for qualitative analysis of fillers and ash for the commoner loading materials, such as clay (hydrated aluminum silicate), talc (hydrated magnesium silicate), barium sulfate, barium carbonate, calcium sulfate, and calcium carbonate, are well known and are included in the TAPPI Standards. To test for Ti place about 0.5 gram of the ash in a 250-ml. beaker, add 20 ml. of concentrated H_2SO_4 and 10 grams of $(NH_4)_2SO_4$ and boil for at least 5 minutes. An insoluble residue indicates SiO_2 or siliceous matter. Cool the solution, dilute to 100 ml. with water, heat to boiling, let settle and filter through double Whatman No. 42 paper. Test the filtrate with H_2O_2. A clear yellow or orange color indicates the presence of Ti.

NOTE.—For a more detailed qualitative procedure, see Am. Chem. Soc. Monograph No. 33 "Titanium," by W. M. Thornton.

Quantitative.—The determination of Ti involves its reduction and titration with a ferric salt. The details of the procedure depend upon the other materials present. The general procedure for the determination of TiO_2 is given in Scheme 1, which should be used when none of the other ash constituents are to be determined. Where $BaSO_4$ also is to be determined, use Scheme 3.

The procedure for a complete analysis of the ash *in the absence of* $BaSO_4$ is given in Scheme 2.

Scheme 1: Determination of TiO_2 *Only.*—Weigh out accurately into a 250-ml. beaker a sample of ash containing not more than 0.25 gram of TiO_2. (Usually 0.5 gram is suitable.) Add 20–30 ml. of concentrated H_2SO_4 and 10 grams of ammonium or sodium sulfate. Cover the beaker with a watch glass and carefully boil the contents over a flame for at least 15 minutes. Cool and dilute with water to 125–150 ml. A white precipitate may form, indicating $BaSO_4$. Boil the solution gently and if it contains a precipitate, filter and wash the precipitate with hot dilute H_2SO_4 (1 : 20) and finally with hot water until free from Ti, indicated by testing with 3% H_2O_2 solution, which gives a yellow color with the washings if Ti is present.

NOTE.—Instead of dissolving the ash with concentrated H_2SO_4, it may be fused with Na_2CO_3 in a covered Pt crucible over a Meker burner, using 5–10 grams of dry Na_2CO_3 for 0.5 gram of ash. Digest the melt with 20–25 ml. of concentrated H_2SO_4 in about 125 ml. of water; boil; and filter to remove any $BaSO_4$ and other insoluble matter. Wash the precipitate free of Ti with hot dilute H_2SO_4 (1 : 20) followed by hot water.

The filtrate and washings containing the Ti salts should have a volume of about 250 ml. Reduce and titrate as follows: Drain the Jones reductor to the top of the fine-mesh Zn and add 200 ml. of boiling dilute H_2SO_4 (1 : 20). Slowly drain the reductor and then wash at least four times with boiling water. Drain the reductor to the top of the fine-mesh Zn, wash the hot Ti solution into it and allow it to remain for 15–20 minutes, keeping the reductor covered with a watch glass. During the whole period of reduction pass a slow stream of CO_2 through the receiving flask. Slowly drain the reductor into the receiving flask while CO_2 is continuously passed through it. When the solution has reached the level of the fine-mesh Zn, add more of the boiling dilute H_2SO_4 and bring the level of the solution to the top of the stick Zn. Drain the reductor to the fine-mesh Zn, then wash 4 times with boiling water in the same manner as above. Remove the flask, add 7 ml. of the NH_4SCN indicator and titrate the solution rapidly with the standard ferric alum solution. Calculate the titration to percentage of TiO_2.

NOTES. 1.—In titrating the Ti solution, the greatest accuracy is obtained by adding nearly all of the ferric alum before agitating; then agitate by shaking with a gentle rotary motion which is continued until the final end-point, a light straw color, is reached.

2. Before using the reductor run a blank, using the same concentration of H_2SO_4 in water and the identical procedure as used for the Ti determination, the reduced solution being titrated. This blank should not require more than 0.1 ml. of the standard ferric alum solution. If more is needed, the Zn should be reamalgamated or another lot of ferric alum used.

Scheme 2: Analysis of Ash Containing TiO_2 *in Absence of* $BaSO_4$. (*TiO_2 in mixture with clay, talc, chalk or calcium sulfate.*)

(*a*) *Silica.*—Fuse 0.5 gram of ash with 5–10 grams of Na_2CO_3 in a covered Pt crucible over a Meker burner. Treat the melt with about 125 ml. of dilute HCl (1 : 4), filter, and wash with hot water. Ignite the residue in a tared Pt crucible at the highest heat of a Meker burner, cool in a desiccator and weigh. Treat the ignited and weighed residue with about 5–10 ml. of HF and 3–4 drops of concentrated H_2SO_4, evaporate to dryness on a hot plate and finally ignite to constant weight. If the amount of SiO_2 is considerable, add more

HF and H_2SO_4, and repeat the evaporation and ignition. The loss in weight represents SiO_2.

Evaporate the filtrate from the melt to dryness and bake on the hot plate for about ½ hour to insure complete dehydration of the SiO_2. Take up the residue with warm dilute HCl (1 : 4), filter, and wash with water. Dry the residue, ignite and weigh in a tared Pt crucible. Treat with 5–10 ml. of HF and 3–4 drops of concentrated H_2SO_4, evaporate to dryness on a hot plate and finally ignite to constant weight. The loss in weight represents soluble SiO_2. Add this result to the previous to give the total SiO_2.

If residues are present after the SiO_2 has been removed, fuse with $KHSO_4$, dissolve the melt in dilute H_2SO_4 (1 : 4) and add to the filtrate from the SiO_2 determinations.

(*b*) *Titanium Dioxide and Alumina.*—Add a slight excess of NH_4OH to the combined filtrates and washings from the SiO_2 determination, boil the solution, filter, and wash the precipitate with 5% NH_4OH. Dissolve the precipitate in the original beaker with dilute HCl (1 : 1) and reprecipitate with NH_4OH. Filter through the original filter, and wash, combining the washings with the first filtrate and washings. Dry the residue, ignite to constant weight over a Meker burner and weigh as $Al_2O_3+TiO_2$. Subtracting the TiO_2, as determined in Scheme 1, gives the Al_2O_3. (Any Fe present as an impurity will be weighed as Fe_2O_3 and included with the Al_2O_3.)

NOTE.—Even if Al_2O_3 is not present, a double precipitation is still necessary to insure complete separation of TiO_2, since the gelatinous precipitate tends to absorb appreciable amounts of Ca, Mg, etc. In this case the precipitate may be dried, ignited and weighed as TiO_2.

(*c*) *Calcium Oxide.*—Slightly acidify with HCl the combined filtrates from the TiO_2 and Al_2O_3 separation and adjust the volume to 150–200 ml. Make this solution alkaline with NH_4OH, boil and add an excess of ammonium oxalate solution. Boil gently for about 2 minutes, digest on a steam bath for 1 hour and let cool to room temperature. Filter, wash the precipitate with hot water, dry, ignite strongly, and weigh as CaO.

If preferred, the CaC_2O_4 may be washed free of soluble oxalates, dissolved in dilute H_2SO_4 (1 : 10), heated to 70° C. and titrated with standard $KMnO_4$ solution.

If $CaSO_4$ is present, calculate the CaO weighed or titrated to $CaSO_4$.

Calculation:

$$CaO \times 2.428 = CaSO_4.$$

(*d*) *Magnesium Oxide.*—Adjust the volume of the filtrate from the Ca separation to 150–200 ml. The solution should contain 5 to 10% of NH_4OH. Add an excess of $(NH_4)_2HPO_4$ solution with constant stirring and let stand for at least 4 hours, preferably overnight. Filter the precipitate on a previously ignited and weighed Gooch crucible. Wash with dilute NH_4OH (1 : 1), dry and ignite, slowly at first and finally over a Meker burner, until the weight is constant. (Do not fuse.) Cool in a desiccator and weigh as $Mg_2P_2O_7$. Calculate to MgO.

Calculation:

$$Mg_2P_2O_7 \times 0.3621 = MgO.$$

ANALYSIS OF BISULFITE COOKING LIQUOR[49]

Bisulfite liquor, used in the manufacture of sulfite pulp, consists essentially of a solution of calcium bisulfite, $Ca(HSO_3)_2$, magnesium bisulfite, $Mg(HSO_3)_2$, and free sulfur dioxide, SO_2.

For control tests in the mill, a volumetric analysis is usually sufficient. For a complete analysis, however, gravimetric methods are necessary. Results are usually reported in grams per 100 ml.

Volumetric Control Analysis

Preparation of Sample.—Into a 100-ml. volumetric flask, containing about 50 ml. of water, pipette accurately 10 ml. of bisulfite liquor, holding the tip of the pipette just under the surface of the water. Then dilute the solution with water to the mark and thoroughly mix.

Total SO_2.—Pipette 25 ml. of 0.1 N iodine solution accurately into an Erlenmeyer flask and add about 100 ml. of water. Then pipette 10 ml. of the prepared solution of the sample into the iodine solution and titrate the excess of iodine with 0.1 N thiosulfate solution, adding a little starch indicator solution near the end of the titration if desired. If starch solution is added, the end-point is the disappearance of the blue color. If no starch is used, the end-point is the change from pale yellow to colorless. Subtract the amount of 0.1 N thiosulfate from the original amount of 0.1 N iodine solution (25 ml.) and calculate the difference to grams of SO_2 per 100 ml. of the original sample.

Calculation:

$$1 \text{ ml. } 0.1 \text{ N iodine} = 0.0032 \text{ gram } SO_2.$$

Note.—In control analyses of used or partially used liquors the above procedure may give high results due to dissolved encrusting matter from the wood. In such cases the result obtained should be considered preliminary and a final analysis should be made by adding to the flask an amount of 0.1 N iodine about 5 ml. less than the amount consumed in the preliminary test. Then add 10 ml. of the solution of the sample followed by a little starch indicator and complete the titration with 0.1 N iodine until a blue color appears which is stable for a few seconds.

Free SO_2.—Pipette 10 ml. of the prepared solution of the sample into an Erlenmeyer flask, dilute to about 100 ml. with water and titrate with 0.1 N NaOH solution, using phenolphthalein solution as an indicator and continuing the titration until a pink color is formed which is permanent for 1 minute. Calculate the titration to grams of SO_2 per 100 ml. of the original sample.

Calculation:

$$1 \text{ ml. } 0.1 \text{ N NaOH} = 0.0032 \text{ gram } SO_2.$$

Combined SO_2.—Report the difference between the total SO_2 and the free SO_2, both expressed in grams per 100 ml., as the combined SO_2.

Note.—The free SO_2 is the actual free SO_2 plus half of the SO_2 in the bisulfites of calcium and magnesium, and is more properly called the "available SO_2" as it indicates the SO_2 in excess of the amount necessary to form monosulfites. The combined SO_2 as above calculated represents the SO_2 combined as monosulfites, or in other words is half of the SO_2 in the bisulfites of calcium and magnesium.

[49] T 604 m. Tentative Standard—Dec. 24, 1931. Official Standard—Oct. 2, 1933. Corrected—April 15, 1935.

Complete Gravimetric Analysis

Ordinarily results shall be reported in grams per 100 ml. of the bisulfite liquor. If actual percentages by weight are desired, the figures thus obtained shall be divided by the specific gravity of the original solution.

Silica.—Pipette 25 ml. of the original liquor into a small beaker or porcelain dish and, after adding 5 ml. of concentrated HCl, evaporate the mixture to dryness on the steam bath and dehydrate for 30 minutes at about 130° C. To the residue add 5 ml. of concentrated HCl, and then 100 ml. of hot water. Boil and filter. Wash the residue on the paper thoroughly with hot water, ignite over a Bunsen burner and finally over a blast lamp or Meker burner, then cool and weigh as SiO_2.

Iron Oxide and Alumina.—Dilute the filtrate from the silica determination to about 300 ml., then add 10 ml. of 10% NH_4Cl solution, bring the mixture to a boil and add a slight excess of NH_4OH. After boiling until the odor of NH_3 is nearly but not quite gone, filter the solution, wash the residue thoroughly with hot water, ignite strongly, cool and weigh as $Al_2O_3+Fe_2O_3$.

Calcium Oxide.—Heat the filtrate from the iron oxide and alumina determination to boiling and to it add 20 ml. of 10% $(NH_4)_2C_2O_4$ solution. After allowing the precipitate to settle, filter the solution, wash the residue on the paper thoroughly with hot water, then ignite to constant weight over a Meker burner or blast lamp and weigh as CaO.

Note.—For very accurate work dissolve the original precipitate of CaC_2O_4 through the filter paper with a slight excess of dilute HCl and wash the filter paper with hot water. Then reprecipitate the calcium in the filtrate by boiling with an excess of NH_4OH and a few drops of the $(NH_4)_2C_2O_4$ solution, let settle, filter, wash and ignite.

In the case of a double precipitation, evaporate the second filtrate rapidly to about 25 ml. and add to the first.

Magnesium Oxide.—Evaporate the filtrate (or combined filtrates) from the CaO determination to about 100 ml. and add a slight excess of HCl, followed by 25 ml. of 10% $NaNH_4HPO_4$ solution. Cool the solution and add 25 ml. of concentrated NH_4OH slowly from a burette or dropper with constant stirring. Let the precipitate settle in a cold place for at least 2 hours (preferably over night), then filter on a Gooch crucible containing an asbestos mat which has previously been ignited, cooled and weighed. Wash thoroughly with water containing about 2.5% of NH_3 (1 part concentrated NH_4OH to 9 parts of water), ignite over a Meker burner (not strong enough to soften or melt the pyrophosphate), cool in a desiccator and weigh as $Mg_2P_2O_7$. Calculate to MgO.

Calculation:

$$Mg_2P_2O_7 \times 0.3621 = MgO.$$

Alternative Method for Calcium and Magnesium Oxides.—Pipette 25 ml. of the original liquor into a platinum dish, add about 1 ml. of concentrated H_2SO_4, evaporate the mixture to dryness, carefully ignite, cool and weigh as the mixed sulfates, $CaSO_4+MgSO_4$. Dissolve the residue in 25 ml. of dilute HCl, wash into a beaker, make alkaline with NH_4OH, heat to boiling and add sufficient $(NH_4)_2C_2O_4$ solution to precipitate the lime completely. Continue the boiling for 2 minutes and let the precipitated CaC_2O_4 settle for at least

½ hour. Filter and wash the precipitate thoroughly with hot water, ignite to constant weight over a blast lamp and weigh as CaO. Calculate to $CaSO_4$, deduct the weight from that of the mixed sulfates and calculate the remaining $MgSO_4$ to MgO.

Calculations:

$$CaO \times 2.428 = CaSO_4.$$
$$MgSO_4 \times 0.3349 = MgO.$$

Sulfur Trioxide.—Pipette 50 or 100 ml. of the original sample into a 300-ml. Erlenmeyer flask and completely displace the air above the liquid by a current of CO_2, which has first passed through a wash-bottle containing an approximately 1% solution of $KMnO_4$ to remove any oxidizable sulfur-compounds. Then, with the current of CO_2 still passing into the flask, add 10 ml. of concentrated HCl and evaporate the solution nearly to dryness to remove SO_2. Transfer the solution to a beaker, washing out the flask and adding the washings to the beaker until the total volume is 100–150 ml. Acidify this solution with 2 ml. of concentrated HCl, heat to boiling, and add 10 ml. of 10% $BaCl_2$ solution drop by drop while boiling. Let the precipitate settle for several hours, preferably overnight, filter, wash thoroughly with hot water, ignite, cool and weigh as $BaSO_4$. Calculate to SO_3.

Calculation:

$$BaSO_4 \times 0.3430 = SO_3.$$

Total SO_2.—Determine the total SO_2 by titrating with 0.1 N iodine and thiosulfate as described in the volumetric method.

Calculations.—Calculate the SO_3 to $CaSO_4$ and the CaO to $Ca(HSO_3)_2$. Calculate the MgO to $Mg(HSO_3)_2$. Express the excess of SO_2 beyond that required for the bisulfites of calcium and magnesium as free SO_2.

$$SO_3 \times 1.700 = CaSO_4.$$
$$CaO \times 3.606 = Ca(HSO_3)_2.$$
$$MgO \times 4.625 = Mg(HSO_3)_2.$$
$$Ca(HSO_3)_2 \times 0.6336 = SO_2.$$
$$Mg(HSO_3)_2 \times 0.6872 = SO_2.$$

ANALYSIS OF CASEIN [50]

Commercial caseins are often designated according to the method of preparation, as acid casein, rennet casein, etc. Acid caseins are again subdivided according to the acid used, as sulfuric, muriatic, lactic, etc. This designation was formerly of some value, as the older methods of preparation gave products of different characteristics according to the acid used. With modern methods this is not true and caseins of practically the same properties are now produced with such different acids as lactic and muriatic. The name of a casein, except for the distinction between acid and rennet caseins, therefore gives no hint as to its properties.

Casein is a material for which there is at present no adequate system of testing which can be applied by both producer and consumer. This is due

[50] T 607 m. Tentative Standard—May 26, 1932. Official Standard—Oct. 2, 1933.

to the fact that there is a very wide gap between the information supplied by strictly chemical tests and that necessary to tell how the casein will work in practice. This gap can be bridged only by empirical tests made to duplicate, as nearly as possible, the conditions of actual use, and such tests cannot readily be standardized. Both types of tests are here described.

Sampling.—The usual methods of sampling dried granular material in packages shall be followed, taking equal portions from 2 to 10% of the packages according to the size of the shipment. The composite sample shall be thoroughly mixed, quartered down to suitable size and placed in moisture-proof containers.

Appearance.—The sample should be observed for color, odor, cleanliness and fineness of grinding. There are no exact standards for the first three properties and only experience can enable one to tell whether a sample is up to the desired quality. In general, however, a good casein should be of a creamy yellow color, free from an excessive amount of dark orange-colored particles and visible dirt and of a mild, characteristic odor, neither moldy, musty nor rancid. The fineness of grinding may be determined by screening on standard screens.

Chemical Tests.—***Moisture.***—For accurate work a sample of 3 to 5 grams shall be dried for 5 hours at 98° C. in a vacuum oven. For most work it is sufficiently accurate to dry the sample to constant weight at a temperature of 100–105° C. in an ordinary oven. All weighings shall be made in a glass-stoppered weighing bottle, as casein takes on moisture rapidly when dry.

Fat.—A representative portion of the sample shall be very finely ground and then 5 grams extracted with ether in an extractor of the Soxhlet type. The extraction shall run for at least 16 hours or overnight, collecting the extract in a weighed flask. After evaporating off the solvent, the extracted fat shall be dried to constant weight at not over 100° C.

Routine Method.—A convenient method of moderate accuracy which utilizes the Babcock milk tester is as follows:

Soak 2 grams of the casein in 6 ml. of water in a small beaker and when all particles are thoroughly saturated add, with constant stirring, 9 ml. of concentrated H_2SO_4. Pour the solution into a Babcock milk test bottle (18-gram) and wash out the beaker with a mixture of 5 ml. of water and 5 ml. of concentrated H_2SO_4, adding the washings to the bottle. Fill to the base of the neck with dilute H_2SO_4 (5 : 4) and whirl in a centrifuge for 5 minutes. Then add sufficient hot dilute acid to bring the fat layer completely within the graduated portion of the neck and whirl for 2 minutes. While still hot read the amount of fat on the graduated neck. As the bottle is designed for a charge of 18 grams, this reading multiplied by 9 will give the percentage of fat in the casein.

Ash.—Weigh about 2 grams of casein into a large porcelain crucible and ignite over a low flame until complete carbonization has taken place, being careful that the contents of the crucible do not burst into flame. Then ignite over a burner or in a muffle until the ash is white or very light gray, cool in a desiccator and weigh. The final ignition should be at as low a temperature as is consistent with obtaining a white ash. The procedure should not be carried out in platinum as this metal is attacked by the phosphorus in the casein.

If oxygen is available the operations may be carried out in a Rose crucible and the final ignition assisted by a stream of oxygen.

Alkali.—Add about 5 ml. of distilled water to the ash and warm. Then add a drop or two of phenolphthalein indicator and if the ash is alkaline titrate it with 0.1 N HCl until colorless; then add 2 drops of methyl orange and complete the titration to a pink color. Calculate the total titration to Na_2O.

Calculation:

1 ml. 0.1 N HCl = 0.0031 gram Na_2O.

NOTE.—The ash of a pure casein should not be alkaline to phenolphthalein or to methyl orange. If it shows alkalinity, test it qualitatively for borax, sodium carbonate and sodium phosphate.

Starch.—Warm a portion of the sample with water. Cool and add a few drops of very dilute iodine solution. A blue color indicates starch.

NOTE.—If added alkali has been found in the casein, make the solution slightly acid before adding the iodine solution.

Total Acidity.—Weigh 20 grams of casein into a beaker and add 100 ml. of water. After soaking for a short time titrate with 1.0 N or 0.5 N NaOH, running in a little at a time and warming on the steam bath after each addition until the end-point is reached. Litmus paper, moistened and dipped into the hot solution shall be used as an indicator and the end-point shall be considered as reached when blue litmus is turned very slightly red and red litmus is turned very slightly blue. Report the result as percentage of NaOH required to neutralize the casein.

Calculation:

1 ml. 1.0 N alkali = 0.04 gram NaOH.

Soluble Acidity.—Soak 20 grams of the casein in 200 ml. of water at room temperature for at least 1 hour, filter and titrate 50 ml. of the filtrate with 0.1 N NaOH, using methyl orange indicator. Report the acidity as the number of ml. of 0.1 N alkali required to neutralize 1 gram.

Nitrogen.—The nitrogen is not usually determined in casein except for some special purpose. When it is desired the usual Kjeldahl method should be used.

NOTE.—Authorities differ as to the factor for converting N to casein and it is known to differ with different lots of casein. According to Browne, N×6.38 will give the percentage of pure casein: while Höpfner and Burmeister state that N×6.61 will give the fat-, ash-, and moisture-free casein present. To convert to commercial, air-dry casein as received, the factors have been found to vary from 7.69 to 9.10 for different samples. It is suggested that the factor 8.00 be arbitrarily selected and assumed to apply in all cases where it is desired to convert nitrogen to commercial air-dry casein.

Empirical Tests.—***Insoluble Matter.***—Weigh 100 grams of casein into a liter beaker, add 300 ml. of water and stir thoroughly. After about 10 minutes add a solution of 15 grams of Na_2CO_3 (soda ash) in 100 ml. of water and stir until thickening takes place. Put the beaker in a water bath at a temperature of about 60° C. and let it stand, with occasional stirring, for 3 hours. At the end of this period add 400 ml. of boiling water and stir thoroughly for about 5 minutes. Pour the solution upon a small brass, 200-mesh sieve which has been weighed to 0.1 mg. and soaked in boiling water. Wash the sieve and residue thoroughly with boiling water, then dry and weigh. Report the percentage of insoluble matter.

Solubility (Cutting Test).—Weigh 50 grams of the ground casein into a 350-ml. beaker and add 7.5 grams of powdered borax. Add 250 ml. of water at a temperature of 70° C. and heat at this temperature on the water bath for 15 minutes, stirring constantly. High-grade caseins will dissolve completely, while inferior samples will show more or less insoluble materials of various kinds. (It should be noted that a casein may not be completely soluble by this test, yet be entirely satisfactory for coating purposes when more alkali is used.)

Viscosity.—Viscosity tests are of considerable help in determining whether a casein is satisfactory for coating purposes, but it is nearly impossible to standardize the methods employed. In the first place, there is no fixed relationship between the viscosity of a casein solution and that of a coating mixture made from it, and as the coating mixture is what interests the coater it is quite useless to test the casein solution only. In the second place, the viscosity of a coating mixture varies with the kind of clay, the kind of satin white, the proportion of the two in the mixture and the kind and amount of solvents used in dissolving the casein. Unless standard grades of clay and satin white can be distributed for testing purposes the best that can be done is for each user to work up a test which suits the conditions in his own particular plant.

Clay-Carrying Strength.—In the case of casein used in the coating of paper, strength may be considered to be the number of parts of clay which one part of casein will hold on the surface of the paper with just sufficient strength so that the coating will not be removed during the printing of the paper. (Different mineral matters require different amounts of casein, but for testing purposes clay has been generally adopted.) The following method is recommended:

Soak 50 grams of casein in 190 ml. of a solution containing 7 grams of Na_2CO_3 and warm on the steam bath until solution is complete. Add sufficient water so that the total weight of solution is 250 grams and 1 gram of casein is present in 5 grams of solution. It makes practically no difference what alkali is used as a solvent provided the solution is complete and not overheated for any length of time.

Into a heavy porcelain or enamel-ware cup weigh 100 grams of coating clay which has been dried at 100° C. or higher, and to this add 70 ml. of water. When it has soaked for a short time, stir until free from lumps. This can be done very conveniently by means of a copper spatula which is bent nearly at right angles on the end to form a foot with which lumps may be pressed out and broken up. Balance this cup with its contents of clay, water and spatula on a balance which is sensitive to 0.1 gram with a load of 500 grams, and then add 30 grams of the hot casein solution. Mix thoroughly and spread a little of the mixture thinly and evenly on a sheet of paper similar to that used for coating purposes. Replace the cup on the balance, add 5 grams of casein solution, mix and again spread on a sheet. Repeat this process until it is certain that enough casein has been added to give a coating of sufficient strength. The sheets will then represent increments of 1 gram of casein, the first being 6 grams per 100 of clay, the second 7 grams, etc. Mark the sheets 6, 7, 8, etc. If care is taken not to spill or waste any of the coating mixture during the test, the amount used for making each sheet will not introduce any appreciable error.

The coated sheets should be dried in the air at room temperature until fully dry and tested with sealing wax for strength. For this test heat a stick of sealing wax on one end until it almost drips and press the hot end firmly down on the surface of the coated paper. When it is fully cold and hard pull it off with a quick, vertical pull. When doing this the paper must be held firmly; this may be done by using a large washer which will fit over the wax and hold the paper down entirely around it. If insufficient casein is used, the coating will pull off without taking any fiber with it; while if excess casein is used, the surface of the wax will be entirely covered with coating to which fibers are adhering. There is generally an intermediate " critical point " when the central area of the wax shows fibers and the edges coating only. This would be considered just on the line between weak and strong.

The test should be reported as the number of pounds of clay held by one pound of casein in the coating which gives the critical point. This figure is obtained by dividing 100 by the number of grams of casein required to give the critical point.

NOTE.—The results obtained by this test are influenced by the kind of clay used as well as the kind of paper to which the coating mixture is applied. Of still greater importance is the thickness of coating applied and it has been proved that for accurate work it is necessary to keep the weight per ream of coating constant within 1 pound on either side of the desired amount. This cannot be accomplished by spreading the coating with a brush or even by means of a hand scraper, and the only satisfactory solution is to construct a machine which will apply a very uniform and controllable amount.

ANALYSIS OF SALT CAKE [51]

The principal use of salt cake in the pulp and paper industry is in the manufacture of sulfate pulp. Salt cake is an anhydrous sodium sulfate which contains varying amounts of impurities. The principal impurities usually are sulfuric acid, common salt, and sulfates of Fe, Al, Ca and Mg. " Chrome Salt Cake," obtained as a by-product in making chromic acid, has a yellow color and contains $Na_2Cr_2O_7$ (and/or Na_2CrO_4).

A complete analysis of salt cake is somewhat complicated and involves a considerable number of determinations, as outlined below. Since some mills are mainly interested in the acidity and the Na_2SO_4 content, directions for a " short analysis " are also given.

Preparation of Sample.—Mix the sample thoroughly, breaking down or grinding any lumps; quarter down to about 100 grams; grind the quartered portion, if necessary, to about 60-mesh or finer; and place in a separate stoppered bottle.

Complete Analysis

Moisture.—Weigh 10 grams of the prepared sample in a flat-bottomed dish of porcelain, glass or platinum and dry to constant weight at 100–105° C. (Four hours is usually sufficient.) Let the dish and contents cool in a desiccator before weighing and make the final weighing rapidly. Calculate the loss in weight to percentage and report as Moisture.

[51] T 619 m. Tentative Standard—Nov. 2, 1933. Official Standard—April 15, 1935.

Insoluble Matter.—Weigh 50 grams of the prepared sample into a 400- or 500-ml. beaker. Add about 250 ml. of boiling water and stir well for 5–10 minutes. Filter at once through a filter paper which has been previously dried at 105° C., cooled and weighed in a weighing bottle, collecting the filtrate in a liter volumetric flask. Wash the residue and the filter paper thoroughly with hot water until a few drops of the washings give no test for sulfates. Place the filter paper and contents in the weighing bottle and dry to constant weight at 100–105° C. Calculate the percentage of insoluble matter.

Cool the filtrate and washings in the liter flask to room temperature, dilute to the mark at 20° C. and mix thoroughly. Call this Solution *A*.

Acidity.—Pipette 100 ml. of solution *A* (equivalent to 5 grams of the sample) into a beaker or flask, dilute with an equal volume of water, add about 1 ml. of phenolphthalein indicator, and titrate to a pink color with 0.1 N NaOH. Calculate the titration to percentage of H_2SO_4 and report as Acidity, calculated as H_2SO_4.

Calculation: 1 ml. 0.1 N NaOH = 0.0049 gram H_2SO_4.

NOTE.—This titration gives the total acidity or alkali-consuming power, and includes not only the free H_2SO_4 present in the material but also the acidity due to sulfates of Fe and Al, and of any bichromate. The actual free H_2SO_4 may be closely approximated by calculating the amount of H_2SO_4 due to the various impurities and subtracting from the percentage of acidity as H_2SO_4.

Factors: H_2SO_4 equivalent = Al_2O_3 $\times 2.89$
= FeO $\times 1.36$
= Fe_2O_3 $\times 1.84$
= $Na_2Cr_2O_7$ $\times 0.375$

Chloride.—To the solution which has been titrated for acidity add a drop or two of methyl orange or methyl red indicator, make very slightly acid with a few drops of dilute H_2SO_4, and bring back to neutrality by adding about 1 gram of powdered $CaCO_3$ and stirring. Set the flask on a white surface or transfer the contents to a porcelain dish; add 10 drops of K_2CrO_4 indicator solution (10%) and titrate with 0.1 N $AgNO_3$ until the brick-red coloration due to Ag_2CrO_4 remains just visible after stirring. Calculate the titration to percentages of Cl and NaCl (and also to the equivalent of Na_2O for use in the final calculations).

Calculations: 1 ml. 0.1 N $AgNO_3$ = 0.00355 gram Cl.
= 0.00585 gram NaCl.
= 0.00310 gram Na_2O.

Ferrous Iron.—To 5 grams of the original prepared sample in an Erlenmeyer flask add 100 ml. of warm water and 5 ml. of concentrated H_2SO_4. Warm on the steam bath a few minutes, just long enough to dissolve all soluble matter. Cool under a water tap and titrate at once with 0.1 N $KMnO_4$. Calculate the titration to percentages of FeO and $FeSO_4$ (and also the equivalent of Fe_2O_3).

Calculations: 1 ml. 0.1 N $KMnO_4$ = 0.0072 gram FeO.
= 0.0152 gram $FeSO_4$.
= 0.0080 gram Fe_2O_3.

Ferric Iron.—Pipette 100 ml. of solution *A* (equivalent to 5 grams of the sample) into a 250-ml. beaker, add a few drops of concentrated HNO_3, cover with a watch glass, and boil a few minutes to oxidize the Fe. Add 5 ml. of concentrated HCl or about 1 gram of NH_4Cl. Then add slowly dilute NH_4OH in slight excess. Boil until the odor of NH_3 is nearly but not quite gone, filter, and wash the residue thoroughly with hot water. Save the filtrate. Place the filter paper in a weighed platinum crucible; dry in an oven; smoke off the filter paper; ignite the residue over a Meker burner to constant weight; and calculate the percentage of $Fe_2O_3+Al_2O_3$.

Add about 2 grams of $KHSO_4$ to the residue in the crucible and fuse quietly over a gentle heat until the melt is clear. Dissolve the melt in warm water, dilute to about 100 ml., add 5 ml. of concentrated H_2SO_4, and pass the hot solution through a Jones reductor to reduce the Fe. Cool the reduced solution and titrate at once with 0.1 N $KMnO_4$. Calculate the percentage of total Fe in terms of Fe_2O_3 and subtract the amount of Fe_2O_3 equivalent to the FeO previously determined. The difference is the ferric Fe in terms of Fe_2O_3. (Calculate also the equivalent amount of $Fe_2(SO_4)_3$.)

Calculations: 1 ml. 0.1 N $KMnO_4=0.008$ gram Fe_2O_3.
$Fe_2O_3\times 2.50 = Fe_2(SO_4)_3$.

Alumina.—Subtract the percentage of total Fe in terms of Fe_2O_3 from the percentage of mixed oxides, $Fe_2O_3+Al_2O_3$, and report the difference as Alumina. (Calculate also the equivalent amount of $Al_2(SO_4)_3$.)

Calculation: $Al_2O_3\times 3.36=Al_2(SO_4)_3$.

Lime.—Heat the filtrate from the Fe and Al hydroxides to boiling and add 2 ml. of concentrated NH_4OH and 10 ml. of 4% $(NH_4)_2C_2O_4$ solution. Let stand one-half hour or until the precipitate settles clear. Filter and wash thoroughly with hot water. Char off the filter paper in a weighed platinum crucible and finally ignite to constant weight over a Meker burner. Cool in a desiccator and take the final weight rapidly. Calculate the weight to percentage of CaO. (Calculate also the equivalent amount of $CaSO_4$.)

Calculation: $CaO\times 2.43=CaSO_4$.

Note.—If preferred, instead of igniting the CaC_2O_4 to CaO and weighing, the CaC_2O_4 may be titrated with 0.1 N $KMnO_4$ as described in the method for Analysis of Limestone.

Magnesia.—Acidify the filtrate from the lime determination with HCl, concentrate to about 150 ml. and heat to boiling. Add 10 ml. of saturated $NaNH_4HPO_4$ solution and boil for several minutes. Cool to room temperature and add NH_4OH drop by drop with constant stirring until the crystalline precipitate begins to form; then add a moderate excess and continue stirring for several minutes. Let stand in a cool place overnight and filter on a Gooch crucible, previously ignited and weighed. Wash with dilute NH_4OH (1 : 10) containing a few drops of concentrated HNO_3, ignite in a muffle, cool in a desiccator and weigh as $Mg_2P_2O_7$. If a muffle is not available, place the Gooch crucible in a larger platinum crucible and ignite directly over a flame. Do not use sufficient heat to fuse or melt the precipitate. Calculate to percentage of MgO. (Calculate also the equivalent amount of $MgSO_4$.)

Calculations: $Mg_2P_2O_7 \times 0.362 = MgO$.
$Mg_2P_2O_7 \times 1.08 = MgSO_4$.

Chromium Trioxide.—Pipette 100 ml. of solution *A* (equivalent to 5 grams) into an Erlenmeyer flask. Add 5 ml. of concentrated HCl and 10 ml. of 10% KI solution, and titrate the free iodine with 0.1 N $Na_2S_2O_3$ solution. When the yellow-brown color has nearly disappeared, add a little starch indicator solution and continue the titration to the disappearance of the blue color. From the titration calculate the percentage of CrO_3 and of $Na_2Cr_2O_7$. (Calculate also the equivalent amount of Na_2O.)

Calculations: 1 ml. 0.1 N $Na_2S_2O_3 = 0.00333$ gram CrO_3.
$= 0.00437$ gram $Na_2Cr_2O_7$.
$= 0.00207$ gram Na_2O.

Total Soda.—(*a*) ***Chrome Salt Cake.***—To 100 ml. of solution *A* in a 500-ml. beaker add 10 ml. of alcohol and 10–15 ml. of concentrated HCl and boil down to half volume to reduce the Cr and remove the bulk of the alcohol. To the hot solution add a slight excess of NH_4OH and 10 ml. of 4% $(NH_4)_2C_2O_4$ solution. Boil until the odor of NH_3 is nearly gone; let stand about 15 minutes; filter and wash thoroughly with hot water, collecting the filtrate and washings in a 250-ml. volumetric flask. Discard the precipitate which contains the Al, Cr, Fe and Ca. Cool the solution, dilute to 250 ml. at 20° C., and mix thoroughly. Call this solution *B*.

Pipette 50 ml. of solution *B* (equivalent to 1 gram of the sample) into a weighed dish, preferably of platinum; evaporate to dryness on the steam bath; and ignite carefully to avoid spattering, gradually raising the heat until no more fumes of NH_4-salts or SO_3 come off. After cooling the residue moisten it with about 2 ml. of dilute H_2SO_4 and repeat the evaporation and ignition in order to convert any chloride to sulfate. Cool, moisten the residue with a freshly prepared, nearly saturated solution of $(NH_4)_2CO_3$ in water; again evaporate on the steam bath and ignite strongly over a Meker burner. Cool in a desiccator, weigh, and calculate to percentage.

The residue is $Na_2SO_4 + MgSO_4$. Subtract the percentage of $MgSO_4$, previously determined, and calculate the difference to Na_2O.

Calculation: $Na_2SO_4 \times 0.4364 = Na_2O$.

(*b*) ***Ordinary Salt Cake.***—In the absence of Cr, omit the preliminary boiling with alcohol. Heat 100 ml. of solution *A* to boiling; add 10 ml. of concentrated HCl, then a slight excess of NH_4OH and 10 ml. of 4% $(NH_4)_2C_2O_4$ solution; and proceed as above.

Sulfur Trioxide.—Pipette 25 ml. of solution *B* (equivalent to 0.5 gram of the sample) into a 400-ml. beaker. Add a drop or two of methyl red and then neutralize the solution carefully with very dilute NH_4OH. To the neutral solution add 300 ml. of water and 2 ml. of dilute HCl (1 : 18), and heat to boiling. Add to the boiling solution 25 ml. of 10% $BaCl_2$ solution, drop by drop from a pipette. Stir well and set aside overnight at room temperature, protected from fumes. Filter and wash with hot water until 25 ml. of the filtrate show not more than a slight opalescence with $AgNO_3$ solution. Place the filter and precipitate in a weighed platinum crucible and heat very slowly and carefully over a low flame to char the filter paper without allowing it to

catch fire. After completing the charring, ignite until white over an ordinary burner, with the crucible uncovered. Cool and moisten the precipitate with a few drops of dilute H_2SO_4. Heat very carefully to drive off the acid and finally ignite to constant weight, cooling between weighings in a desiccator. Calculate the weight of $BaSO_4$ to percentage of SO_3.

Calculation: $BaSO_4 \times 0.3430 = SO_3$.

Final Calculations.—From the total Na_2O subtract the Na_2O equivalent to the NaCl and to the $Na_2Cr_2O_7$; calculate and report the remaining Na_2O as Na_2SO_4.

From the total SO_3 subtract the SO_3 equivalent to the Na_2SO_4, $Al_2(SO_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$; calculate and report any excess of SO_3 as free H_2SO_4. (The SO_3 equivalent of each of the sulfates is obtained by subtracting the corresponding oxide percentage from the sulfate percentage; e.g., 1.52% $FeSO_4$ −0.72% FeO = 0.80% SO_3.)

Form of Report.—It is suggested that the results of a complete analysis to be reported in the following form:

	Per Cent
Moisture, loss at 100° C.	.....
Insoluble in Water	.....
Acidity, calculated as H_2SO_4	.....
Chloride, Cl	.....
Ferrous Oxide, FeO	.....
Ferric Oxide, Fe_2O_3	.....
Alumina, Al_2O_3	.....
Lime, CaO	.....
Magnesia, MgO	.....
Chromium Trioxide, CrO_3	.....
Sulfur Trioxide, SO_3	.....

Combined as follows:

Sodium Chloride, NaCl	.....
Sodium Bichromate, $Na_2Cr_2O_7$	.....
Aluminum Sulfate, $Al_2(SO_4)_3$	.....
Ferrous Sulfate, $FeSO_4$	.....
Ferric Sulfate, $Fe_2(SO_4)_3$	.....
Calcium Sulfate, $CaSO_4$	.....
Magnesium Sulfate, $MgSO_4$	.....
Sodium Sulfate, Na_2SO_4	.....
Free Sulfuric Acid, H_2SO_4	.....

Short Analysis

Prepare the sample as previously described, except that it may be quartered down to about 25 grams before the final grinding.

Acidity.—Weigh 5 grams into a 300-ml. Erlenmeyer flask, add 100 ml. of hot water and heat until all soluble matter has dissolved. Cool under a water tap and pour into a 500-ml. porcelain dish, using 100 ml. of water in small portions to rinse the flask and complete the transfer. Add about 1 ml. of phenolphthalein indicator and titrate to a pink color with 0.1 N NaOH. Calculate the titration to percentage of H_2SO_4 and report as Acidity, calculated as H_2SO_4.

Calculation: 1 ml. 0.1 N NaOH = 0.0049 gram H_2SO_4.

Sodium Chloride.—Follow the procedure previously described under Chloride. Calculate the titration to percentage of NaCl, and also to the equivalent amount of Na_2SO_4.

Calculation: $NaCl \times 1.215 = Na_2SO_4$.

Sodium Bichromate.—If the material contains Cr, warm a 5-gram sample with 100 ml. of water in a 300-ml. Erlenmeyer flask until all soluble matter is dissolved, cool to room temperature and proceed as described previously under Chromium Trioxide. Calculate the percentage of $Na_2Cr_2O_7$ and also the equivalent percentage of Na_2SO_4.

Calculation: $Na_2Cr_2O_7 \times 0.542 = Na_2SO_4$.

Sodium Sulfate.—Treat 5 grams of the sample in a 500-ml. beaker with 100 ml. of hot water, 5 ml. of concentrated HCl and a few drops of concentrated HNO_3, and stir until all soluble matter is dissolved. Boil a few minutes to oxidize the Fe. If the material contains Cr, add 10 ml. of alcohol and boil down to half volume. Then add a slight excess of NH_4OH and 10 ml. of 4% $(NH_4)_2C_2O_4$ solution and proceed as previously described under Total Soda. Calculate the percentage of the final residue, which contains all the Na as Na_2SO_4 and all or part of the Mg as $MgSO_4$. (The latter is usually very small and is disregarded.) Subtract the Na_2SO_4 equivalent of the NaCl and of the $Na_2Cr_2O_7$, and report the difference as Sodium Sulfate.

ANALYSIS OF ROSIN [52]

Rosin is the residue obtained after distilling off the volatile matter from turpentine gum. It is graded according to color. The higher the temperature to which the distillation is carried, the darker is the resulting product. The common commercial grades, in the order of their color, from the palest and best to the cheapest and darkest, are: X, WW, WG, N, M, K, I, H, G, F, E, D, and B. Grades G, F, and E are most frequently used in the paper industry. The acid number is generally considered the best index, in selecting rosin for making rosin size. Other tests which give valuable data for certain purposes are saponification number, unsaponifiable matter, toluol-insoluble matter, and ash.

Sampling.—Rosin is usually received in wooden barrels of 500 pounds gross weight or metal drums containing a gross weight of 280 pounds. These containers are stripped off, leaving a solid block of rosin. The sample for test should be taken from approximately the center of the block. Ordinarily it is sufficient to sample two containers selected at random from a shipment. In cases of dispute the number of containers to be sampled shall be mutually agreed upon. The sample shall be reduced to laboratory size by crushing to pass a half-inch sieve, mixing and quartering. The final laboratory sample shall be prepared *immediately before analysis* and shall consist of approximately 200 grams. It shall be ground to pass a No. 10 sieve, mixed thoroughly and placed in a wide-mouthed bottle of such a size that it will be completely filled with the powdered rosin.

NOTE.—As rosin has a marked tendency to oxidize very rapidly, samples should be kept in lump form as much as possible.

Color Grade.—To determine the color grade of rosin a set of standard cubes

[52] T 621 m. Tentative Standard—Feb. 19, 1934. Official Standard—April 15, 1935.

must be available. These may be obtained from D. C. Campbell, Jacksonville, Fla.; also from Harris M. King, P. O. Box 333, Savannah, Ga.

Melt the rosin under examination and cast in a sheet iron mold to form a cube of the same dimensions as those in the standard set. Care must be taken to heat the rosin only just enough to pour, as overheating darkens the color. After the cube has solidified, compare it as to color with the standards by looking through the cubes in daylight toward a neutral sky (not blue).

Acid Number.—Dissolve 3 grams of rosin by warming with about 100 ml. of alcohol which has previously been neutralized by adding a few drops of phenolphthalein solution and then 0.1 N NaOH until it is faintly pink. When the rosin has dissolved, titrate the solution to a pink color with 0.5 N NaOH, adding more phenolphthalein if necessary. Express the result in terms of milligrams of KOH (not NaOH) consumed per gram of rosin. This is the Acid Number. It is also sometimes customary to report the percentage of acid. This should be calculated as abietic acid.

Calculation: 1 ml. 0.5 N NaOH = 28.06 mg. KOH = 0.1511 gram abietic acid.

Saponification Number.—Weigh duplicate 2-gram portions of the powdered rosin into Erlenmeyer flasks of about 300-ml. capacity. Add to each 25 ml. of 0.5 N alcoholic KOH solution. In a third flask place 25 ml. of the 0.5 N alcoholic KOH (as a blank determination). Connect the flasks to reflux condensers and boil for 2 hours, swirling them from time to time to prevent the rosin from sticking to the sides of the flask above the liquor line. Cool and titrate the contents of each flask with 0.5 N HCl and phenolphthalein to the disappearance of the pink color. From the titration of the blank subtract the titration of each sample and report the number of milligrams of KOH consumed by 1 gram of the rosin as its Saponification Number.

Calculation: 1 ml. 0.5 N KOH = 28.06 milligrams.

Ester Number.—The ester number is the difference between the saponification number and the acid number.

Unsaponifiable Matter.—(*a*) ***In Alcoholic Solution.***—Saponify 5 grams of the sample by boiling for 2 hours under a reflux condenser with an excess (about 50 ml.) of 0.5 N alcoholic KOH. Evaporate most of the alcohol, add about 100 ml. of water and extract in a separatory funnel with 25 ml. of acid-free ether. Draw off the watery layer into a second separatory funnel, extract this with a second 25-ml. portion of acid-free ether and add the ether extract to that in the first funnel. Wash the combined ether extracts with two 25-ml. portions of water, adding the wash waters to the solution in the other funnel. Pour the washed ether extract into a weighed Soxhlet flask. Finally extract the water solution a third time with 25 ml. of ether, first using the ether to rinse out the funnel which contained the ether extracts. Draw off the water layer into another separatory funnel and wash the third ether extract twice with water. Pour this washed ether extract into the flask containing the main ether extract. Distill off the ether and dry the flask and contents at not over 105° C. to constant weight, cooling in a desiccator before weighing. Calculate the percentage of unsaponifiable residue.

(*b*) ***In Aqueous Solution.***—Saponify 5 grams of the sample by boiling for 4 hours under a reflux condenser with 1 gram of Na_2CO_3 dissolved in 50–75 ml. of water. Cool the solution and extract with acid-free ether as above.

NOTE.—The residue as determined in (*a*) represents the true unsaponifiable matter. The residue obtained in (*b*), however, represents more nearly the rosin which is unacted upon in determining the acid number and, since rosin size is made with soda ash, it is considered to be the unsaponifiable matter so far as size-making purposes are concerned.

Ash.—Ignite 5 grams of the powdered rosin in a weighed platinum crucible to a white or light gray residue. Cool in a desiccator and weigh. Calculate to percentage.

Toluol-Insoluble Matter (1).—The toluol-insoluble matter is a measure of foreign dirt—chiefly sand, chips, dirt and bark. In many cases the determination of dirt is not necessary. Where it is important, the following method shall be used:

Place 50 grams of the *freshly* powdered sample in a 300-ml. beaker, add 150 ml. of toluol, free from water and non-volatile residue, and dissolve the sample with the aid of heat and occasional shaking. When no particles of rosin are visible, filter at once through a porcelain Gooch crucible which has been previously prepared with a mat of pure, well washed asbestos, and has been finally washed thoroughly with the toluol, dried in the oven at 105° C. for 30 minutes, cooled in a desiccator, and weighed. If the rosin filtrate is not clear, return it through the crucible until clear, finally washing the residue and the outside of the crucible free from rosin with additional hot toluol. Dry the crucible and contents to constant weight in the oven at 105° to 110° C. (one hour usually suffices), cool in a desiccator, weigh, and calculate the percentage of toluol-insoluble matter.

Literature Cited

1. Am. Soc. for Testing Mat. Standard D 269–30.

POISONS

THEIR DETECTION AND ESTIMATION

With Special Reference to Organic Poisons [1]

Samples for toxicological examination should be placed in clean glass jars, having airtight glass covers. The jars should be sealed, numbered and labeled, and the sealer should affix his initials. The portions of the body to be preserved for the chemical examination are, as a rule, the stomach and contents, a portion or all of the intestinal tract, about one fourth of the liver, both kidneys, the spleen, the brain, the bladder contents, and occasionally the heart, lungs and a portion or all of the spinal cord.

A preliminary examination should precede the analysis, noting the appearance, odor, color, and reaction to litmus of the samples. Opium, hydrocyanic acid, carbolic acid, chloroform, alcohol, nitrobenzole, benzaldehyde and nicotine may be suggested by the odor.

Salts of copper, portions of insects, or certain arsenical preparations or other coloring matter may be suggested by the color.

The lining of the stomach should be examined; corrosion may indicate caustic alkalies, acids, or other corrosive substances; a reddening of the lining may indicate cyanide; a " toughened " stomach lining may indicate mercury salts.

The color of the blood should be noted, red indicating possible hydrocyanic acid or carbon monoxide poisoning.

The odor of such poisons as hydrocyanic acid and chloroform can often be detected better in the brain than any other portion of the body.

All available information as to symptoms should be obtained and considered since this information will usually point to a particular class of poison or even to a particular poison. Thus the work of the identification may be lessened and, what is more important, valuable and unreplaceable material will not be wasted in useless tests. It is usually safe to assume that but one poison is present. However, a quantity of a poison insufficient to cause death may be found, in which case the examination should be continued.

Food materials suspected of containing poisons may be examined by the methods given but it is well to remember that in cases of intentional poisoning the quantity of poison is usually large and the analyst should not be misled by finding traces, as of arsenic, for instance, which might easily occur in a food material due to the very common practice of using arsenical spray on fruits and vegetables.

[1] By Arthur R. Maas, Professor of Pharmacy and Toxicology, University of Southern California.

Classification of Poisons

Nearly all of the common poisons may be placed in one of three groups:

Group I. Poisons volatilized without decomposition by distillation with steam from an acid solution.

Group II. Organic poisons. Most of the poisons in this group can be separated from extraneous matter by treatment with hot alcohol containing tartaric acid. Alkaloids, glucosides, bitter principles and many organic compounds come in this group.

Group III. All poisonous metals.

NOTE. Caustic alkalies, mineral acids, and a few special poisons such as oxalic acid do not adapt themselves to the above scheme and will have to be treated separately.

General Procedure

Organs of the human body should first be weighed and then a representative weighed sample reduced to a finely divided mass (a clean small meat grinder answers nicely for this purpose).

It is advisable always to preserve a portion of the material in its original form for possible further examination.

About one tenth of the thoroughly mixed material is used in testing for each one of the three groups, the balance being reserved for checking. If only a small amount of the original material is available, tests for all three groups of poisons may be made with the same portion. In this case, after removal of volatile poisons, the residue should be divided into two unequal portions, the larger being used for non-volatile organic poisons and the smaller, together with the residue from the non-volatile organic, for metallic poisons.

Blank tests should be run upon *all* reagents used and the chemist should familiarize himself with the various tests before applying them to the unknown. At least three confirmatory tests, different in character, should be applied to the unknown substance before the presence of a poison can be definitely established. Whenever possible these confirmatory tests should include form, color, odor or taste.

Group I

Place some distilled water in a clean round-bottomed flask connected with a Liebig condenser. Distil about 10 ml. and test distillate with silver nitrate solution. Absence of a precipitate indicates that the apparatus is clean. Next pour out the distilled water and transfer a weighed portion of the finely divided and thoroughly mixed material to the flask, adding enough distilled water for free distillation. Then add tartaric acid solution gradually until the mixture is acid after thorough shaking. The distillate should be received in a test tube in which a little distilled water has been placed. The distillate may contain:

Yellow Phosphorus
Hydrocyanic Acid
Chloroform
Ethyl Alcohol
Methyl Alcohol
Acetone
Iodoform
Nitrobenzene
Carbolic Acid
Aniline
Chloral Hydrate
Carbon Disulfide
Benzaldehyde
Amyl Nitrite
Amyl Alcohol

Collect the distillate in several portions. Test the first portion of 5–10 ml. for hydrocyanic acid, chloroform, ethyl alcohol, methyl alcohol, acetone, iodoform and nitrobenzene. The other portions of 10–20 ml. will contain the less volatile substances, carbolic acid, etc. Observe the reaction of the distillate; if acid, test for hydrocyanic acid. Observe the odor of the distillate. A number of the above substances have characteristic odors. When there is reason to believe that a certain substance is present, confirm the results by making other characteristic tests. It is seldom necessary to test for all members of the group. Test a portion of the first distillate with silver nitrate T. S. Failure to obtain a precipitate eliminates hydrocyanic acid.

Yellow Phosphorus

Average dose, 1/120 grain.

Lethal dose, 1/8 to 1½ grains.[2]

Preliminary Test: (Sherer's Test.)—Place the finely divided material in a small flask and cover with water if necessary. Suspend in the neck of the flask by means of a cork with a V-shaped slit two prepared strips of filter paper in such a manner as to avoid touching the sides of the flask. One strip is moistened with $AgNO_3$ solution and the other with a solution prepared by adding an excess of NaOH solution to a solution of a lead salt. Warm the flask gently to 40°–50° C. on a water bath. If both strips darken, phosphorus may be present together with H_2S. If the $AgNO_3$ strip darkens and the Pb strip does not, phosphorus *may* be present. If neither strip darkens, phosphorus *is not* present. In case there is an indication of phosphorus, proceed as follows:

Make a separate portion of the finely divided material quite liquid with water to which a little H_2SO_4 has been added to neutralize any NH_3 present. Transfer to a flask or retort fitted with a long condenser terminating in a receiver containing a dilute solution of $AgNO_3$. The distillation is carried out in a darkened room. Phosphorus may be detected by a phosphorescent ring at the point where the vapors are condensing. Care must be taken to avoid reflections of light which may be taken for phosphorescence. If a distinct phosphorescence is observed, it is positive proof that elementary phosphorus is present, but the absence of phosphorescence is not a good negative test, as many substances like alcohol, oil of turpentine, H_2S, etc., may entirely prevent this indication. If the preliminary test is positive and no indication is obtained on distillation, more complete works like Autenrieth or Witthaus should be consulted for further tests which include elementary phosphorus, phosphorous, and hypophosphorous acids.

Hydrocyanic Acid

Average dose of 2% U. S. P. acid, 1½ minims.
Lethal dose of 2% U. S. P. acid, 40 minims.
Lethal dose of anhydrous acid, 6/10 to 9/10 grain.

[2] Where doses are given, it means average adult doses. The lethal dose given represents the amount that would under average conditions probably be fatal to an adult.

In testing for hydrocyanic acid examine the brain, the contents of the stomach and intestines, and organs rich in blood such as the liver, and heart. Examination should be made as soon as possible, as hydrocyanic acid rapidly disappears through volatilization and combination with sulfur of proteins during putrefaction forming sulfocyanates.

Note cautiously the odor of the material as well as the odor of the distillate. Hydrocyanic acid has a characteristic " peach kernel " odor.

Apply the following tests:

1. *Schonbein-Pagenstecher Test*

In case of suspected cyanide poisoning this test should precede the distillation. A small quantity (15 grams) of the finely divided material is placed in a small flask together with enough tartaric acid solution to moisten it thoroughly and a piece of guaiac-copper " paper " [3] is suspended in the neck of the flask in such a manner as not to touch the liquid. The flask and contents are then gently warmed on the water bath. If the paper is not turned blue or bluish green, it is positive proof that neither HCN nor a readily decomposed cyanide is present. A positive test means only that HCN or cyanide *may* be present as many substances such as Cl, HCl, NH_3 and HNO_3 produce this same change in color.

2. *Prussian Blue Test* [4]

To a small portion (3 ml.) of the distillate in a test tube add a few drops of KOH solution, then 1 or 2 drops of a $FeSO_4$ solution and 1 drop of a $FeCl_3$ solution. Shake and warm gently. Acidify with dilute HCl. If cyanide is present in quantity a precipitate of Prussian blue will appear immediately, but if present only in traces the solution will acquire a blue or bluish green color which on standing 10 to 24 hours will throw down a flocculent precipitate of Prussian blue. The maximum sensitivity of this reaction is 1 : 5,000,000.

Since formaldehyde is the principal ingredient of most embalming fluids, the Prussian blue test cannot be relied upon as a negative test when working with embalmed tissues.

3. *Sulfocyanate Test*

To another portion of the distillate in a small evaporating dish add 2 or 3 drops of KOH solution, enough yellow ammonium sulfide to color the solution yellow and evaporate to dryness on the steam bath. Dissolve in a few drops of water and acidify with a little dilute HCl. Filter through a double filter paper into another small evaporating dish. Add 2 or 3 drops of dilute $FeCl_3$ solution. If HCN is present in the distillate, a reddish to blood-red color will appear, which is discharged upon the addition of a few drops of $HgCl_2$ solution. The color so produced is due to ferric sulfocyanate. The maximum

[3] "Guaiac-copper" paper is prepared by saturating strips of filter paper with a freshly prepared 10% alcoholic tincture of resin of guaiac, drying and, just before using, moistening with a 1 to 1000 $CuSO_4$ solution.

[4] The author has found that hydrocyanic acid fails to respond to this test in the presence of formaldehyde, due probably to the following reaction:

$$HCOH + HCN = HOCH_2CN.$$

sensitivity of this test is 1 : 4,000,000 and is not affected by the presence of formaldehyde.

4. *Silver Nitrate Test*

Acidify 1 ml. of the distillate with dilute HNO_3 in a small test tube and add 2 or 3 drops of $AgNO_3$ sloution. If HCN is present, a white curdy precipitate resembling that of AgCl is produced which dissolves in NH_4OH. This reaction cannot be due to HCl because when a very dilute solution of HCl is distilled HCl is not found in the distillate. The maximum sensitivity of this test is 1 : 250,000.

5. *Silver Cyanide Crystal Test*

Acidify 1 ml. of the distillate with dilute HNO_3 in a small test tube. Place a drop of dilute $AgNO_3$ on a microscope slide and carefully invert the drop over the center of the tube so as to avoid touching the side of the tube. Allow to stand for 15 to 20 minutes, then cover with a coverglass and examine under the microscope, using a power of from 50 to 100 diameters. If HCN is present, characteristic crystals of AgCN will appear under the microscope. (See Fig. 283.)

6. *Detection of Hydrocyanic Acid in the Presence of Potassium Ferrocyanide*

Should the material contain potassium ferrocyanide (which is not a poison), the ordinary tartaric acid distillation will show the presence of HCN even though there is none present before distillation. Therefore, in medico-legal cases where cyanide is found it is well to test the original material for potassium ferrocyanide as follows:

Shake a small portion with water, filter and test with $FeCl_3$ and dilute HCl for the Prussian blue reaction. If there is an indication of a ferrocyanide, distil a fresh portion of the material with an excess of $NaHCO_3$ and repeat the tests for cyanides.

7. *Detection of Mercuric Cyanide*

In cases of suspected mercuric cyanide poisoning a few ml. of a freshly prepared saturated aqueous solution of H_2S should be added to the contents of the flask and distillation continued. If mercuric cyanide is present, HCN will be found in this second distillation. This step is made necessary because mercuric cyanide in dilute solution is not decomposed by either tartaric acid or sodium bicarbonate.

8. *Estimation of Hydrocyanic Acid*

When HCN is found, it is always well to determine as accurately as possible the amount present.

Acidify a weighed portion of the material with sulfuric or tartaric acid and distil into dilute NaOH free from chlorides. Determine the cyanide in the distillate by a good volumetric method. If chlorides are present in the distillate, they may be removed by one redistillation over borax.

Chloroform

Average dose, 5 minims.
Lethal dose by inhalation, from 15 drops up.
Lethal dose by mouth, 2 to 8 drachms.

Distribution: When inhaled, chloroform passes from the air into the blood-plasma, then to the red blood corpuscles. It can often be found in the brain.

Phenylisocyanide Test

To a small portion of the distillate add 1–2 drops of aniline oil and a few ml. of KOH solution and heat gently. If chloroform is present, the offensive, characteristic odor of phenylisocyanide is produced. This test is sensitive to 1 in 5000. This odor is produced by other substances such as chloral and chloral hydrate and for this reason other tests should be applied.

Schwarz's Resorcinol Test

To 2 ml. of a 5% solution of resorcinol add a few drops of NaOH solution and a small portion of the distillate and heat to boiling. If chloroform is present even in small quantity, a yellowish red color is produced. Chloral, bromal, bromoform, and iodoform also give this test.

Nicloux's Method (Quantitative)

To 20 ml. of blood or other aqueous liquid add about 95 ml. of alcohol and 5 ml. of a 5% solution of tartaric acid in alcohol. Distil 40 ml. into 10 ml. of alcohol, using a condenser with an adapter dipping beneath the surface of the alcohol so that none of the chloroform may be lost. To the distillate add 10 ml. of a 10% alcoholic solution of KOH (free from chlorides) and boil under a reflux condenser for 30 minutes, cool, add 15 ml. of distilled water, neutralize to phenolphthalein with dilute H_2SO_4, add a few drops of neutral potassium chromate solution and titrate with standard silver nitrate solution.

$$3Cl = 1CHCl_3;\ CHCl_3 + 4KOH = HCOOK + 3KCl + H_2O.$$

Ethyl Alcohol

Lethal dose, 3½ to 7 fluid ounces.

Distribution: Ethyl alcohol may be found in the brain, liver and blood.

Detection

1. *Lieben's Iodoform Test*

Warm a small portion of the first distillate to 40° or 50° C. Add 1–2 ml. of an aqueous iodo-potassium iodide solution and enough KOH solution to give a distinct yellow to brownish color. If alcohol is present, a yellowish white to lemon yellow precipitate of iodoform is formed. If the solution is very dilute, some time may be required to form the precipitate. When formed slowly the crystals may be identified under the microscope. This test is very delicate but is not characteristic of ethyl alcohol because other primary alcohols (except

methyl alcohol) and many secondary alcohols produce this reaction. (See Fig. 281.)

2. *Chromic Acid Test*

Warm a small portion of the distillate with dilute H_2SO_4 or HCl and add 1–2 drops of a very dilute $K_2Cr_2O_7$ solution. The color of the liquid will change from red to green and give off the odor of acetaldehyde. Many other volatile organic compounds react in this manner.

3. *Ethyl Acetate Test*

Mix a small portion of the distillate with an equal volume of concentrated H_2SO_4. Add a very small quantity of anhydrous sodium acetate and heat. The odor of ethyl acetate is produced if alcohol is present.

4. *Vitali's Test*

Thoroughly mix a small portion of the distillate in a glass dish with a small piece of solid KOH and 2 or 3 drops of CS_2. Let stand a short time without warming. When most of the CS_2 has evaporated add a drop of ammonium molybdate solution and then an excess of dilute H_2SO_4. A red color is produced if alcohol is present. Acetone and acetaldehyde will produce a similar color. A 5% solution of alcohol gives this test distinctly.

Methyl Alcohol (Wood Alcohol)

Fatal dose, 1 fluid ounce.

Methyl alcohol is found in methylated spirit, which contains 10 parts methyl alcohol and 90 parts ethyl alcohol. It is also found in some other forms of denatured alcohol. It may poison either from external application or internal administration. One teaspoonful has produced blindness and one ounce death.

Detection

To 5 ml. of the first distillate add 1 ml. of 25% H_2SO_4 and 4 ml. of N/5 $KMnO_4$; allow to stand 10 minutes and filter. (Decolorize with H_2SO_3 if necessary.) To 5 ml. of the filtrate add 1 drop $FeCl_3$ solution and about 5 ml. milk. Underlay this mixture with concentrated H_2SO_4. A violet ring at line of contact indicates formaldehyde (oxidation product of methyl alcohol).

To the balance of the filtrate (5 ml.) add 8 drops of an aqueous solution of resorcinol (1–200) and then carefully pour this upon 5 ml. of concentrated sulfuric acid contained in a test tube in such a manner that the two liquids do not mix. After standing for three minutes a rose-red ring at line of contact indicates formaldehyde (oxidation product of methyl alcohol).

Carbolic Acid (Phenol)

Average dose, 1 grain.
Fatal dose, 1–4 drachms.

Distribution: Carbolic acid is very rapidly absorbed by the skin and gastro-

intestinal tract and appears in the liver, stomach, blood, kidneys, brain and urine in a very short time after taking.

1. If present in quantity, this acid may be recognized by its odor.

2. *Millon's Test*

Heat 1 ml. of the distillate with a few drops of Millon's Reagent. (See Special Reagents.) If carbolic acid is present even in minute quantity, a distinct red color is produced. The absence of this color is an excellent indication of the absence of phenol but other substances such as the three cresols and salicylic acid may produce this color and for this reason other tests should be applied if this test is positive.

3. *Bromine Test*

To 1 ml. of the distillate add 1 or 2 drops of freshly prepared saturated bromine water. If phenol is present in quantity a yellowish white precipitate is immediately thrown down, but if highly diluted some time may be required. The precipitate should be examined under the microscope for characteristic crystals of tribromphenol. (See Fig. 282.)

Phenol in a dilution of 1 : 50,000 yields on standing a precipitate containing some of the characteristic crystals.

Substances like salicylic aldehyde and salicylic acid also produce this precipitate and other tests should, therefore, be applied.

4. *Ferric Chloride Test*

To a small portion of the distillate add a very dilute solution of $FeCl_3$ drop by drop. If phenol is present to the extent of 1 : 1000, a blue-violet color is produced. Dilute HCl and H_2SO_4 change the color to yellow. This test is entirely negative in the presence of mineral acids.

5. *Hypochlorite Test*

Add a little NH_4OH to a small portion of the distillate and then 2–3 drops of freshly prepared solution of calcium or sodium hypochlorite and warm. If phenol is present in quantity a blue color is produced, but if very dilute only green or blue-green color appears. The maximum sensitivity of this reaction is 1 : 1000.

6. *Nitrite Test*

To a small portion of the distillate add a few drops of a dilute alcoholic solution of ethyl nitrite and underlay the mixture in a test tube with concentrated H_2SO_4. If phenol is present, a red zone will appear at the point of contact of the two liquids. The maximum sensitivity of this reaction is 1 : 10,000.

7. *Quantitative Estimation of Phenol*

For the quantitative estimation of phenol the analyst is referred to the Beckurts-Koppeschaar Volumetric Method as described in Autenrieth-Warren, " The Detection of Poisons and Powerful Drugs," page 31.

Chloral Hydrate

Average dose, 8 grains.
Fatal dose, ½ to 2 drachms.

Distribution: Chloral hydrate may be found in the stomach, blood, brain and spinal cord.

Detection

Chloral hydrate gives the phenylisocyanide and resorcinol test for chloroform but the distillate does not have the characteristic odor of chloroform.

Add a few drops of Nessler's solution to a small quantity of the second distillate and shake. If chloral hydrate is present, a yellowish red precipitate is produced which on standing changes to dirty yellowish green. Formaldehyde gives a brownish precipitate with this reagent. Boil a small portion of the distillate with 0.2–0.3 g. solid sodium thiosulfate. If chloral hydrate is present, a turbid liquid of brick red color is produced. A few drops of KOH solution will remove the turbidity and change the color to brownish red.

Decomposition of Chloral Hydrate

Heat a small portion of the distillate with calcined MgO for 30 minutes on the steam bath with a reflux condenser. The chloral hydrate is decomposed into magnesium formate and chloroform. Test as follows:

Distil a few ml. of the decomposed liquid and test the distillate for chloroform. Filter the residue, concentrate to a small bulk and divide into two parts. To one part add 1–2 drops of $HgCl_2$ solution and warm. Formic acid reduces $HgCl_2$ to HgCl, producing a white precipitate. To the other part add 2–3 drops of $AgNO_3$ solution and warm. Formic acid reduces $AgNO_3$ to metallic silver, depositing a mirror on the test tube.

Group II

Alkaloids, Glucosides and Other Organic Compounds

Alkaloids form salts with tartaric acid insoluble in ether and chloroform but soluble in alcohol and water. These alkaloidal salts are decomposed by alkalies liberating the alkaloid which is insoluble in water, but soluble in ether or chloroform. The above is the principle by which alkaloids are separated from foreign material.

Method of Analysis

The substance is finely hashed, if solid, and then treated with several volumes of purified alcohol [5] and made slightly acid with tartaric acid. The mixture is placed in a flask and heated under a reflux condenser for about 30 minutes. After cooling it is filtered and the residue washed with purified alcohol. The alcoholic extract is evaporated on a water bath to the consistence of a syrup. From 3 to 4 volumes of purified alcohol are then gradually stirred in, the solution allowed to stand an hour or more, filtered and carefully evapo-

[5] The alcohol used should be purified by treating it with about 0.1% of tartaric acid, allowing to stand 24 hours and then distilling.

rated on a water bath to a thin syrup. This syrup is now treated with about 50 ml. of distilled water and filtered.

NOTE.—If croton oil or nitroglycerine are suspected, they should be looked for in the residue insoluble in water.

The filtered aqueous acid solution should be placed in a separatory funnel and extracted with ether, and the extractions repeated until the ether on evaporation gives no residue.

Unite the ether extractions, wash once with a small quantity of water, filter through dry paper and evaporate. The residue may contain:

Fats and Oils	Acetanilid	Antipyrine
Ptomaines	Phenacetine	Salicylic Acid
Picrotoxin	Chloretone	Benzoic Acid
Colchicine	Brometone	Veronal
Picric Acid	Essential Oils	Trional
Menthol	Cantharidin	Sulfonal
Camphor	Caffeine	
Phenol		
Cresol		
Thymol		

Note the general appearance and taste of the residue. If bitter, test for picrotoxin and colchicine. Veronal and trional have a bitter taste and give characteristic crystals. Sulfonal is tasteless and gives prismatic crystals.

The aqueous liquid is next rendered slightly alkaline with NaOH and extracted with ether as before.

The extracted substances from which the solvent has been evaporated should be weighed so as to determine the amount present. If material so recovered is crystalline, the weight may be taken as representing the actual amount present. If not crystalline, the extract may be purified in most cases by dissolving in dilute acid, making the solution alkaline as before and re-extracting with the volatile solvent.

The residue from the evaporation of the ether may contain any of the following substances:

Ptomaines	Atropine	Codeine	Antipyrine
Coniine	Hyoscyamine	Narcotine	Quinine
Nicotine	Scopolamine	Pilocarpine	Caffeine
Aniline	Cocaine	Sanguinarine	
Toluidine	Physostigmine	Berberine	
Veratrine	Brucine		
Strychnine	Hydrastine		

Carefully acidify the aqueous alkaline residue remaining from the preceding ether extraction with dilute HCl and then make alkaline with dilute NH_4OH, using litmus paper for both tests. Extract repeatedly with hot chloroform containing 10% by volume of alcohol.

The residue from the evaporation of the chloroform may contain:

Morphine
Apomorphine
Narceine

Acetanilid

Dose, 2–10 grains.
Lethal dose, 60 grains has proven fatal, less is dangerous to a person with a weak heart.

Phenylisocyanide Test

Dissolve a small portion of the residue in 5–6 ml. of a boiling solution of alcoholic potash. Cool, add 2 or 3 drops of chloroform and again heat. If acetanilid is present, the offensive odor of phenylisocyanide is produced. The alcoholic potash decomposes acetanilid into aniline and potassium acetate. The former with chloroform gives phenylisocyanide.

Bichromate-Sulfuric Acid Test

To a small portion of the residue add 1–2 drops of concentrated H_2SO_4 containing a little $K_2Cr_2O_7$. Acetanilid produces a red color changing to brown and finally dirty green.

Veronal

Dose, 8 to 15 grains.
Lethal dose, 120 grains has proven fatal.

Distribution: Veronal should be looked for in the stomach and bladder contents.

Fig. 275.—Atropine 1 : 500. With Wagner's Reagent.

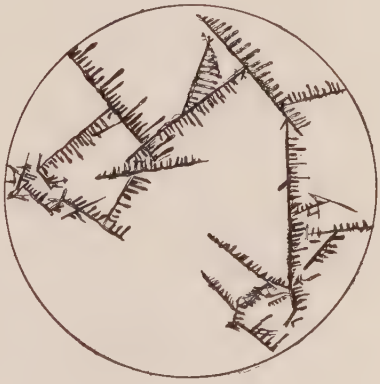


Fig. 276.—Cocaine 1 : 1000. With Gold Chloride.

Fig. 277.—Codeine 1 : 200. With Marme's Reagent.

Fig. 278.—Narcotine 1 : 1000. With Sodium Carbonate.

Fig. 279.—Nicotine 1 : 1000. With Gold Chloride.

Fig. 280.—Strychnine 1 : 500. With Ammonium Thiocyanate.

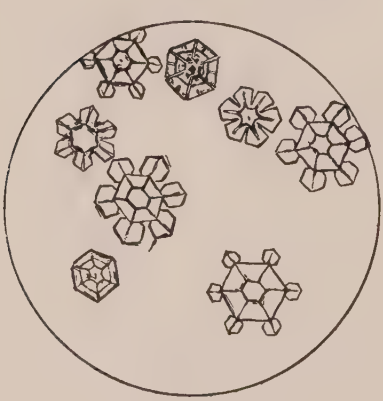


Fig. 281.—Iodoform Crystals.

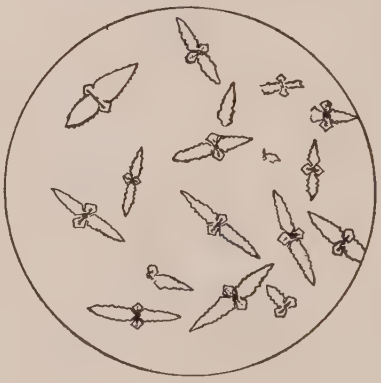


Fig. 282.—Tribromphenol Crystals.

Fig. 283.—Silver Cyanide Crystals.

Fig. 284.—Morphine Crystals.

Purification and Detection

Dissolve a portion of the residue from the acid ether extraction in the smallest possible quantity of hot water. If colored, decolorize by boiling a few minutes with animal charcoal, filter hot and allow the solution to cool. If no crystals are deposited, evaporate further and cool. Make the following tests on any pure crystals obtained:

Dissolve a few crystals in a few drops of water and test with sensitive litmus paper. An aqueous solution of veronal has a faintly acid reaction.

Dissolve a few crystals in a few drops of dilute NaOH solution and acidify the clear solution with dilute HCl. Veronal is precipitated.

Determine the melting point on a few of the crystals. Pure veronal melts between 188° and 189° C.

Mix a few of the crystals with a few crystals of pure veronal and determine the melting point of the mixture. The mixture should have the same melting point as the unknown if the unknown is pure veronal. Carefully sublime a number of the crystals in a dry test tube and compare with crystals known to be pure veronal. A low power microscope is used for this purpose. Fuse some of the crystals with metallic sodium in a dry test tube. Cool, dissolve carefully in water and test for sodium cyanide by the methods given on pages 1945–1947. Veronal contains nitrogen which reacts to form sodium cyanide.

Extraction of Veronal from the Bladder Contents

Evaporate a considerable quantity of the urine on the steam bath to 1/5 its volume and extract several times with ether, using a large volume for each extraction because veronal is not very soluble in this solvent. Evaporate the extract and proceed with the residue as directed under "Purification and Detection" given above.

Nicotine

Dose, 1/20 to 1/10 grain.
Lethal dose, 2–3 drops pure alkaloid.

Distribution

Nicotine should be sought in the stomach, lungs and liver.

Detection

If present in large quantities, nicotine may be detected by its odor. If nicotine is suspected, the ether extract from NaOH solution should be evaporated without heat. If nicotine is present, oily drops of a colorless or yellowish liquid which reddens phenolphthalein and has a peculiar odor somewhat resembling stale tobacco smoke will remain in the residue. If exposed to the light, the oil becomes yellow or brown, thicker and finally resinous. If heated, it volatilizes completely, giving off white fumes.

If a drop of HCl be placed on a watch glass and inverted over a similar watch glass containing nicotine alkaloid, a white cloud is produced which is, however, not so dense as that produced by coniine under like conditions and no crystals are produced as with coniine.

Place a drop of an aqueous extract of the oily residue on a microscope slide, add a drop of a solution of gold chloride, let stand for several minutes and examine under the microscope. If nicotine is present, small characteristic crystals will appear upon standing.

QUININE

Dose 15 grains.

Detection

Fluorescence Test

Dissolve a portion of the residue in a little dilute sulphuric acid. If quinine is present, this solution will exhibit a vivid blue fluorescence.

Thalleioquin Test

Dissolve a portion of the residue in a few drops of very dilute acetic acid and add few drops of saturated chlorine or bromine water and follow with excess of ammonium hydroxide. The liquid acquires an emerald-green color.

Herapathite Test

To a small portion of the residue add 20 drops of an acid mixture (30 drops of acetic acid, 20 drops of absolute ethyl alcohol and 1 drop of dilute sulphuric acid) and heat to boiling. Finally add 1 drop of an alcoholic solution of iodine (1 : 10). When the solution has stood for a few minutes, green leaflets with a metallic luster will form.

STRYCHNINE

Dose, 1/60 to 1/12 grain.
Minimum lethal dose for an adult, ½ grain.

Distribution

Strychnine should be looked for in the stomach and contents and organs rich in blood such as the liver and heart.

Detection

Strychnine has a very bitter taste and may be detected even in a dilution of one in 700,000 by the taste.

Bloxam's Test

Add 1–2 drops concentrated HNO_3 to a portion of the solid residue in a porcelain dish and gently warm. On adding a small crystal of $KClO_3$, a scarlet color is produced if strychnine is present. NH_4OH changes the color to brown and a brown precipitate falls. On evaporating slowly to dryness, a dark green residue is left. This residue is soluble in water, forming a green solution which is changed to orange-brown by KOH and green again by HNO_3. This reaction distinguishes strychnine from any of the alkaloids commonly occurring in cases of poisoning.

Bichromate Test

Place a drop of an acid extraction of the residue on a microscope slide and add a drop of a dilute solution of $K_2Cr_2O_7$. Let stand for a few minutes and examine under the microscope. If strychnine is present, characteristic crystals will be found. Dry the crystals and add a drop of concentrated H_2SO_4, holding the slide over a white surface. A deep blue color which changes through deep violet, purplish red, orange to yellow is produced if strychnine is present.

NOTE.—A mixture of hydrastine and morphine causes this same color reaction but this mixture is not possible if the extractions have been properly carried out.

Sulfocyanate Test

Place a few drops of the acid extraction on a microscope slide and add a drop of a dilute solution of ammonium sulfocyanate. Strychnine sulfocyanate produces characteristic needle-shaped crystals.

BRUCINE

Dose, 1/12 to ½ grain.

Detection

Dissolve a small quantity of the residue in 1 or 2 drops of concentrated HNO_3. If brucine is present, a blood red color will appear, which soon changes to yellowish red and finally to yellow. Add a few drops of a freshly prepared dilute solution of stannous chloride to the yellowish red or yellow solution. An intense violet color will appear. Heat usually changes this color to yellowish red but more stannous chloride solution restores the violet color.

Dissolve a small portion of the residue in 2 drops of dilute HCl. Place a drop of this solution on a microscope slide and add a drop of platinum chloride solution. If brucine is present, characteristic rod-like crystals separate and may be compared under the microscope with those produced in a solution of brucine. These crystals are formed in solutions as dilute as 1 to 20,000. The best crystals are obtained from the more dilute solutions.

Atropine

Dose, 1/120 to 1/60 grain.
Lethal dose, 1/20 grain. Much larger doses have been followed by recovery.

Detection

Vitali's Test

Dissolve a small portion of the dry residue from the ether extraction of solution made alkaline with NaOH in a few drops of fuming HNO_3 and evaporate to dryness on the steam bath. Cool and moisten the yellowish residue with a few drops of a 4% solution of KOH in absolute alcohol. If atropine is present, an evanescent violet color will appear. This color reaction is also obtained with hyoscyamine, scopolamine, strychnine and veratrine, and therefore other tests should be applied.

Physiological Test

Dissolve a small portion of the residue in a few drops of very dilute H_2SO_4 and place a drop of this solution in a dog's or cat's eye. If atropine is present, a noticeable enlargement of the pupil will be observed. (Note: Great care must be exercised if this test is applied to the human eye.) One drop of a 1 : 130,000 solution of atropine will produce this enlargement.

Dissolve a small portion of the residue in 2 drops of dilute H_2SO_4. Place a drop of this solution on a microscope slide and add a drop of Wagner's Reagent. If atropine is present, an amorphous precipitate appears and slowly forms numbers of small characteristic crystals which may be observed under the microscope. This test is sensitive to 1 in 8000.

Cocaine

Dose, 1/8 to 1 grain.
Lethal dose, 15 grains.

Detection

The material should be examined for cocaine as soon as possible because cocaine undergoes changes in the viscera which are said to change it rapidly into ecgonine.

Dissolve a small portion of the residue in water and touch it to the tongue. Cocaine produces a temporary anesthesia.

To a small portion of the residue in a porcelain dish add a few drops of strong HNO_3 and evaporate carefully to dryness. Treat the residue with a few drops of alcoholic potash and warm. If cocaine is present, a characteristic sweet odor will be given off.

Dissolve a small portion of the residue in 1 or 2 drops of dilute HCl. Place a drop on a microscope slide and add a drop of gold chloride solution. Cocaine produces after a short time very characteristic crystals, the form depending on the dilution. This test is sensitive 1 : 20,000.

Codeine

Dose, ½ to 1 grain.
Lethal dose, 5 grains. Much larger doses have been recovered from.

Detection

Nitric Acid Test

To a small portion of the residue in a porcelain dish add a few drops of a cold 25% solution of nitric acid. Codeine produces a yellow color which soon changes to red. Concentrated nitric acid produces a reddish brown color.

Froehde's Test

To a small portion of the residue in a porcelain dish add a few drops of Froehde's Reagent (see Special Reagents) and warm very gently over a very small flame. Codeine produces a yellowish color which soon changes to green and finally to blue.

Formaldehyde-Sulfuric Acid Test

To a small portion of the residue in a small porcelain dish add a few drops of concentrated sulfuric acid to which has been added a trace of formaldehyde. Codeine produces a reddish violet color which changes to blue-violet.

Marme's Reagent Test

Dissolve a small portion of the residue in 2 drops of dilute H_2SO_4. Place a drop of this solution on a microscope slide and add a drop of Marme's Reagent (see Special Reagents). Characteristic crystals soon begin to form in solution of codeine as dilute as 1 : 2000 and may be observed under the microscope.

CAFFEINE

Dose 3 grains.

Detection

Murexide Reaction

Treat small portion of the residue in a porcelain dish with a few drops of strong hydrochloric acid and a minute crystal of potassium chlorate, and evaporate the liquid to dryness on the water bath. When cold invert the dish over a vessel containing a few drops of ammonia when a characteristic purple coloration is produced.

Theobromine and xanthine give similar reactions to caffeine with an oxidizing agent and ammonia. The purple colorations due to caffeine and theobromine are decolorized by adding alkali hydroxide solution, but that due to uric acid is changed to blue.

Reaction to Alkaloidal Reagents

Caffeine is very imperfectly precipitated by the usual alkaloidal reagents. No reactions result with neutral iodized potassium iodide and Mayer's solution, which behavior distinguishes caffeine from nearly all other alkaloids except theobromine and colchicine. From an acid solution however caffeine is quantitatively precipitated by a solution of iodine and potassium iodide.

Narcotine

Dose, 2 to 15 grains.

Detection

Dilute Sulfuric Acid Test

Dissolve a small portion of the residue obtained from the ether extraction of the NaOH solution in a little dilute H_2SO_4 and evaporate in a small porcelain dish on the steam bath. If narcotine is present, the residue has a reddish yellow color which changes on stronger heating to crimson red. As the acid begins to evaporate, blue-violet streaks radiate from the margin and the entire liquid finally assumes a dirty red-violet color.

Froehde's Reaction

To a small portion of the residue in a porcelain dish add a few drops of Froehde's reagent. If narcotine is present, a greenish color is produced which immediately changes to cherry red. Gentle heat hastens the appearance of the cherry red color which is quite persistent.

Selenious Acid-Sulfuric Acid Test

To a small portion of the residue add a few drops of selenious acid-sulfuric acid reagent (see Special Reagents). If narcotine is present, a greenish steel blue color appears which, after a time, changes to cherry red. Heat destroys the cherry red color immediately.

Sodium Carbonate Test

Dissolve a small portion of the residue in 2–3 drops of very dilute HCl. Place a drop of this solution on a microscope slide and add a drop of a 5% solution of Na_2CO_3. If narcotine is present, small characteristic crystals are precipitated in solutions as dilute as 1 to 20,000. These crystals should be compared under the microscope with crystals obtained from solutions of narcotine of different concentrations.

Morphine

Dose, 1/20 to ½ grain.

Average lethal dose, 1 to 4 grains. Recovery may follow after taking a much larger quantity.

Detection

Formaldehyde-Sulfuric Acid Test

To a small portion of the residue from the chloroform extraction in a small porcelain dish add a few drops concentrated H_2SO_4 containing 2 or 3 drops of 40% formaldehyde solution to 5 ml. acid. A trace of morphine produces a purple red color which changes to violet and finally becomes pure blue. If this test is negative morphine is not present, but a positive reaction must be confirmed by other tests because codeine, heroin and apomorphine produce a similar color.

Froehde's Test

To a small portion of the residue in a porcelain dish add a drop of Froehde's Reagent. Morphine produces a violet color which changes through blue to dirty green and faint red. Other alkaloids of the opium group give similar color reactions.

Iodic Acid Test

Dissolve a small quantity of the residue in dilute H_2SO_4, add a few drops of iodic acid and shake with chloroform. A violet color appearing in the chloroform layer may be due to other reducing agents as well as morphine.

Ferric Chloride Test

Dissolve a small quantity of the residue in dilute HCl and evaporate to dryness on the steam bath. Take up with a few drops of distilled water and add a drop of neutral $FeCl_3$ solution. If morphine is present, a blue color will appear.

Nitric Acid Test

To a small portion of the residue add 1–2 drops of concentrated HNO_3. Morphine gives a blood red color which gradually changes to yellow.

Marme's Test

Dissolve a small portion of the residue in 2 drops of dilute HCl. Place one drop of this solution on a microscope slide and add a drop of Marme's Reagent. If morphine is present in solution to the extent of 1 to 1000, delicate silvery needle-shaped crystals will form slowly around the edges of the drop and in more concentrated solutions these crystals group together to form rosettes as shown in Fig. 284.

OPIUM

Dose, 1 grain.

Lethal dose, 4 grains has produced death. Larger amounts have been recovered from.

The principal constituents of opium are morphine, codeine, narcotine, narceine, and meconic acid.

Narcotine can be extracted from an aqueous solution of opium by shaking out with ether, and evaporating the ether. Meconic acid can be obtained by adding lead acetate to an aqueous solution of opium and filtering off the precipitate of lead meconate (the filtrate will contain morphine acetate). The precipitate of lead meconate is decomposed by treating it with dilute sulfuric acid and gently boiling the mixture, filtering and neutralizing. On adding a drop of ferric chloride solution, a deep red color, not easily destroyed by a solution of mercuric chloride or hot dilute sulfuric acid, indicates meconic acid. Mercuric chloride instantly bleaches the color caused by sulfocyanates while the boiling dilute sulfuric acid destroys that due to acetates by decomposing the acetate and expelling acetic acid.

The solution of morphine acetate should be treated with hydrogen sulfide to remove excess of lead, the solution filtered and the filtrate evaporated to a

soft extract on a water bath. This extract treated with alcohol, filtered and evaporated will give morphine acetate to which the characteristic tests for morphine should be applied.

The presence of morphine, narcotine and meconic acid definitely establishes the presence of opium.

Ptomaines

The consideration of ptomaines is very important in toxicology because of the similarity of these substances to alkaloids. Ptomaines contain nitrogen and are basic in character and may or may not be toxic. They are products of decomposition occurring especially in advanced stages of putrefaction of a dead body. Probably they are always present in cadavers and it seems probable that they are normal products of bacterial life processes.

Great care should be exercised especially in legal-chemical cases not to report an alkaloid present if there is any possibility of the identifying reactions being caused by a ptomaine. No positive report should be made until every characteristic chemical test of the suspected alkaloids has been confirmed, and in case there is even a remote possibility that the suspected substance may be a ptomaine, a physiological test should be made in order to confirm the chemical examination.

A ptomaine may resemble an alkaloid chemically but usually it will have an entirely different physiological action. Ptomaines resembling to a certain degree the following alkaloids have been isolated: atropine, codeine, coniine, delphinine, hyoscyamine, morphine, narceine, nicotine, strychnine and veratrine.

Frequently the resemblance between a ptomaine and an alkaloid lies in one reaction only but an animal decomposition product has been found that resembles morphine in its characteristic solubilities and also liberates iodine from iodic acid but does not give the reactions that are characteristic of morphine alone.

Ptomaines may resemble alkaloids in the following characteristics: they give precipitates with reagents that precipitate alkaloids, their separation with various solvents from both acid and alkaline solution resembles various alkaloids and many ptomaines are strong reducing agents and give the Prussian blue test in common with certain alkaloids.

When it is possible to isolate the alkaloid in a pure state, its identity can be established beyond a doubt.

Group III

This group contains all metals. Arsenic however is best tested for on a small separate portion of the original material.

Preparation of Solution

Place from 50 to 100 g. of the finely chopped material in a 1000-ml. boiling flask. Dilute with water if necessary until a fluid mixture is obtained and add pure concentrated HCl and crystalline $KClO_3$ in the proportion of 25 ml. HCl and 2 g. $KClO_3$ to every 100 g. Allow the mixture to stand cool for 24 hours and heat on the steam bath (preferably under a reflux condenser) with frequent agitation and the occasional addition of $KClO_3$ (0.5 g. at a time) until the contents of the flask are yellow and fluid except for fatty and white granular matter

in suspension and until the liquid does not darken on heating for half an hour without adding $KClO_3$. If, during the heating, the addition of $KClO_3$ does not produce any visible reaction, add more concentrated HCl in the proportion of 10 ml. HCl to every 100 g. material used and continue as directed above. Care should be used to keep the quantities of HCl and $KClO_3$ as small as possible, as an excess of HCl may prevent the precipitation of some of the metals by H_2S. Expel the excess of chlorine by passing a rapid stream of CO_2 through the cool liquid or by adding small quantities of $NaHSO_3$ until a distinct odor of SO_2 is obtained. Filter the solution through a wet filter and wash the residue thoroughly with hot water. If a large amount of fatty residue is left, it should be extracted two or three times with small quantities of hot water acidulated with HCl and these filtered extracts added to the main filtrate. If silver and small quantities of lead, thallium, mercury or barium are suspected, this residue should be examined qualitatively for these metals. If a large excess of HCl is present, add a concentrated solution of Na_2CO_3 to such an extent that the reaction still remains distinctly acid. Place the liquid in a flask fitted with a two-hole rubber stopper and tube dipping below the liquid and pass pure H_2S through it at the temperature of the steam bath for 2 hours. Allow to stand cold for eight or ten hours and filter. A colored precipitate at this stage may mean nothing, as it may be due to organic thio-compounds, and therefore the precipitate and filtrate should be tested by any good method of qualitative analysis for metals.

Detection of Arsenic

Place 10 grams of the finely divided material in a 150-ml. beaker, add 10 ml. of concentrated HNO_3, cover and allow to stand over night. Then add 5 ml. concentrated H_2SO_4 and warm. When the material starts to turn brown, add concentrated HNO_3 1 ml. at a time until SO_3 fumes are given off without the solution turning brown. Cool; carefully add 10 ml. of water and boil down to SO_3 fumes. Cool, dilute, add 0.5 g. KI, warm to 90° C., add dilute solution of $SnCl_2$ to decolorize, cool and run in the regular small Gutzeit apparatus.

Determination of Carbon Monoxide in Air

(Sayers, Yant and Jones, Public Health Reports, Vol. 38, No. 40, Oct. 5, 1923)

The following method slightly abridged from that of the original authors will give approximate results where the percentage of CO in air is less than 0.2%.

Blood Solution

Saturate a small amount of defibrinated blood with CO. This is done readily by passing house gas containing CO through blood for a minute or two or preferably by using air containing 3 to 5% of CO. Prepare a 1 to 20 dilution of this blood with water. Also prepare a 1 to 20 dilution of CO-free blood. For standards set up a series of nine test tubes containing 0.0, 0.2, 0.4 . . . 1.6 ml. of CO-blood dilution, each made up to a final volume of 2 ml. with the CO-free blood dilution. To each of these tubes add 40 mg. of a mixture of equal parts of tannic and pyrogallic acids. Invert the tube 4 or 5 times to mix. These standards give a series in which the proportion of saturation with CO varies from 0 to 80 in steps of 10%. If air is excluded by a paraffin seal on the

surface of the liquid, these standards will be sufficiently permanent for a week or two, but it is little trouble to prepare them fresh for an occasional sample.

A sample of air to be examined is obtained in a 250-ml. bottle, using an aspirator bulb and discharging the bulb at least 25 times into the bottom of the bottle. The bottle is closed with a rubber stopper or with a well-vaselined glass stopper if preferred. Such a sample will keep well. When ready for the test, add to the bottle 2 ml. of the 1–20 CO-free blood dilution, avoiding as much as possible the escape of the air-gas mixture from the bottle. Slowly turn the bottle so that the blood solution flows over the surface of the inside of the bottle, avoiding violent shaking. After 15 or 20 minutes' rotation, transfer the blood solution to a test tube of the same size as the standards, add 40 mg. of the tannic-pyrogallic mixture, invert for mixing as with the standards, and, after standing 15 minutes, compare with the standards and determine the approximate saturation of the blood solution. This may be done with an accuracy of 5% by estimating the degree of color as equal to a standard tube or between two such tubes. The following tables gives the approximate percentage of CO in the air corresponding to the percentage of saturation of the blood when the temperature at the time of making the test is not far removed from 20° C. and the air is otherwise of fairly normal composition, say, containing at least 19% of oxygen.

Saturation %	CO %
0	0.00
10	0.007
20	0.015
30	0.028
40	0.045
50	0.066
60	0.090
70	0.152
75	0.200

Corrections for variations in temperature and composition may be found in the original (loc. cit.).

Determination of CO in Blood

Dilute 0.1 ml. of blood of a supposed victim of CO poisoning to 2 ml. with 0.03% solution of sodium fluoride or 0.05% solution of potassium oxalate (to prevent coagulation). Add 40 mg. of tannic-pyrogallic acid mixture (1–1), invert 4 or 5 times and after 15 minutes compare with standards made up as in the method for CO in air, except that sodium fluoride or potassium oxalate solution of the above strength is used instead of water in making up the blood solutions. Report the percentage of saturation with CO.

In general, slight symptoms may be noted when the hemoglobin of the blood is saturated to the extent of 25%, while 50% saturation gives violent symptoms and a dangerous condition.

Special Reagents

Millon's Reagent

Dissolve 1 part of mercury in 1 part of cold, fuming nitric acid. Dilute with twice the volume of water and decant the clear solution after 24 hours.

Froehde's Reagent

A solution of molybdic acid in sulfuric acid, prepared by dissolving 5 mg. of molybdic acid, or sodium molybdate, in 1 ml. of hot pure concentrated sulfuric acid. This solution, which should be colorless, does not keep long.

Marme's Reagent

Dissolve 30 g. of cadmium iodide and 60 g. of potassium iodide in 180 ml. of water.

Selenious-Sulfuric Acid Reagent

Dissolve 5 mg. of selenious acid ($H_2Se_2O_3$) in 1 ml. of concentrated sulfuric acid.

Iodo-Potassium Iodide Reagent

Dissolve 5 g. of iodine and 10 g. of potassium iodide in 100 ml. of water.

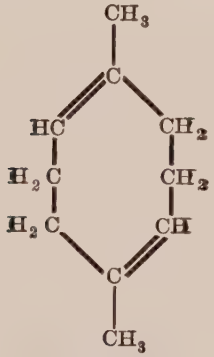
Mayer's Reagent

Dissolve 1.358 g. of mercuric chloride in 60 ml. of water and 5 g. of potassium iodide in 10 ml. of water. Mix the two solutions and dilute to 100 ml.

RUBBER, GUTTA-PERCHA, AND BALATA

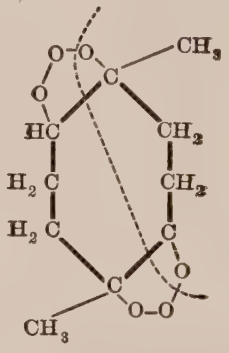
Rubber is obtained from the Latex of certain tropical plants belonging to the Natural Orders, *Euphorbiaceae*, *Apocynaceae*, *Urticaceae*. The Latex is a "milky" juice contained in lacticiferous vessels. It is an emulsoid of rubber in an aqueous serum and is associated with several other substances such as resins, sugars, protein. The chief rubber-bearing plants are: *Hevea brasiliensis* (Parà), *Castilloa*, *Ficus*, and the *Landolphias*. Guayule rubber is obtained from *Parthenium argentatum* (*Compositae*).

The essential constituent of rubber is a hydrocarbon (caoutchouc). It is a polyprene or polymerized terpene $(C_{10}H_{16})_n$.[1] The differences in the physical characteristics of various rubbers are probably due to variations in chemical aggregation, or the value of n, i.e., the degree of polymerization: also the amount and nature of the associated foreign matter. Harries' work on the ozonides of rubber indicates the hydrocarbon to be an unsaturated substance with two ethylene linkages. By bubbling ozone through a solution of caoutchouc in chloroform he obtained an ozonide $(C_{10}H_{16}O_6)_n$, soluble in chloroform.



Rubber hydrocarbon

$+2O_3 \rightarrow$



This splits up on steam distillation into laevulinic aldehyde, laevulinic acid, and a superoxide.

The formula indicates that the rubber hydrocarbon is an 8 carbon ring compound with two double bonds and that there are two methyl groups attached to the ring. The systematic name for the rubber hydrocarbon is "1.5 dimethyl-cyclo-octadiene 1.5." The term octadiene signifies an 8 C-ring with two ethylene linkages. The 1.5 at the end refers to the position of the bonds in the ring whilst the 1.5 at the beginning of the expression refers similarly to the position of the methyl groups. Other formulae for the rubber hydrocarbon have been proposed, and the formula is still an open question.

[1] Many investigators prefer the formulae $(C_5H_8)_y$; $(C_5H_8Br_2)_x$, etc.

Chapter by L. E. Salas.

1966

The **rubber hydrocarbon** is capable of forming compounds with certain reagents. These compounds are generally addition products (except the nitrosite, $C_{10}H_{15}O_7N_3$). $C_{10}H_{16}Br_4$, $C_{10}H_{16}O$, and $C_{10}H_{16}S_2$. The process of vulcanization is based on the combination of sulfur with rubber.

Rubber is a colloid, and is not strictly soluble; it forms pseudo-solutions or swellings. A colloid (suspension or emulsion) is represented by suspended particles (solid or liquid) which by carrying like (+ or −) electrical charges, repel one another continuously, and thus refuse to settle by gravity. These particles exhibit the " Brownian movement."

The addition of an electrolyte neutralizing the electric charges causes the particles to coalesce (coagulation), whereupon they settle out. A colloid solution appears as a mass of particles which, on greater dilution, decrease in size, disappearing as individuals to form a " sol " apparently limpid although the beam of light as employed in the ultramicroscope discovers solid particles.

The first effect of the " solvent " is to swell the hydrocarbon, forming a network or sponge.

The principal solvents for rubber are gasoline, carbon-disulfide, petroleum-ether, benzene and its homologues, carbon-tetrachloride, chloroform, turpentine.

Crude Rubber, as it appears on the market, is the product of the coagulation of the latex. Coagulation is brought about by various methods, chiefly by " smoking " as in the case of wild rubbers from the Amazon and smoked sheet, or by means of dilute acetic acid for plantation crêpe rubber. In the latter instance the coagulum produced is passed through rollers to consolidate it into thin sheets.

In both cases such rubbers contain, besides the hydrocarbon, about 2–3% of substances soluble in acetone and designated as " Resins " (which contains various ingredients, including fatty acids). Rubber also contains varying amounts of protein (2–6%) and sugars (inositol), etc., and of course moisture and dirt. The chief objects of analysis are:

1. To provide information in order that the manufacturer may exercise efficient control of the raw material.
2. To test whether the manufactured articles meet specifications.

Examination of Raw Rubber.—The following information concerning a consignment of rubber may be required:

1. Origin, botanical source, method of collection, process of coagulation, details of packing and despatch.
2. The gross weight at time of dispatch, gross weight at time of sampling, average tare, condition of the packages at unloading in dock.
3. The method of sampling is an important point to be decided between buyer and seller. Storage plays an important part as regards ship consignments, for rubber stored in ships' holds near the engine-room would be much drier than in other situations. (The rubber is also likely to suffer serious deterioration if overheated.)
4. The washing loss, the content of washed dried rubber, its appearance, color, odor, and strength after removal from the vacuum pans.

5. The percentage nitrogen content of the dried rubber, the percentage of acetone extract and amount of ash.
6. Quantity of caoutchouc (pure).
7. Results of trial vulcanizations.

Evaluation of Latex.—The price of latex is governed entirely by the actual ***percentage of dry rubber*** it contains (per cent by weight, or lbs. per gallon of latex). It is important to obtain a truly representative sample. The most convenient method for determining the quantity of rubber in latex is the trial coagulation method. The conditions have become standardized and are stated thus (see Stevens, *I. R. I. Transactions,* Vol. V, **5**, 1930): " A portion of the representative sample (10–50 ml.) is weighed out into a porcelain evaporating basin. To this is added very dilute acetic acid (½–1%) with constant stirring. A little practice soon indicates the stage to which acidification must be carried and the basin is then placed on the steam bath. On leaving undisturbed for about half an hour, the rubber will set to a coherent coagulum from which the clear serum may be poured off and replaced by clean water. The clot is then taken to the washing rollers and crêped out thinly under a good stream of water. Drying may be effected in a steam oven, but is preferably performed at a somewhat lower temperature, e.g., 70° C. or even 50° C."

" Revertex "—a concentrated latex introduced by Dr. E. A. Hauser—is evaluated in a similar manner.

Determination of Ammonia (used as a preservative of latex).—Dilute the latex with distilled water and titrate with N/100 acetic acid using an external indicator.[2] Other determinations are rarely required, but examination for traces of metals such as copper, manganese, cobalt, chromium and iron (which might cause serious deterioration in the finished product) may be important. Their detection is carried out on the ash and reference should be made to special tests for traces of the metals mentioned.

Raw Rubber (wild and plantation) appears on the market as sheets, blocks, slabs or scraps. Each kind of rubber possesses a characteristic odor due to the contained " resins," decaying protein matter or the material used for coagulation.

The vegetable refuse, earthy impurities, moisture and soluble substances (organic acids, carbohydrates, tannins, etc.) may in some cases together constitute more than 50% of the whole, and which are removed by the washing and drying process (residual moisture about 0.5%). Plantation rubber is more carefully prepared and arrives clean, and being comparatively dry (as sheet, crêpe, or blocks) requires little or no further treatment. Washed and dried raw rubber has a density of about 0.91–0.97. It is highly elastic but hardens when cooled down to 0° C. and softens if heated above 60° C. Above 100° C. in the presence of air, it becomes gradually converted to a black viscous fluid. However, rubber may be heated out of contact with air to higher temperatures and on cooling resumes to a large degree its former condition.

Technical Analysis of Crude Rubber (for factory control and evaluation) comprises the determination of washing loss, true rubber content, resin, ash. The sampling of crude rubber must be carefully done as time spent on careful

[2] Hydrochloric acid and methyl red indicator may be used.

analysis may be wasted by bad sampling. Laboratory samples should not be less than 20 lbs. One sample should be taken from each case unless the packages are many and are much alike when every third or fifth package may be sufficient. In this case it is a good plan to wash and dry samples from the first half of the range and compare with results obtained in the other half. If the results for washing loss agree within 1%, take the mean. By using a long bladed knife or toothless " saw " a wedge-shaped sample having its apex at the center may be cut; or in the case of a prismatic block the best sample is obtained by cutting out a quarter. A slice through the center may involve a large error. It is sometimes found that the rubber contains so little moisture or is so tacky that cutting may be troublesome. Under these circumstances the knife must be wetted and the superfluous water removed afterwards. In sampling wild rubbers containing much debris, a sample of 100 lbs. should be passed through the factory washing process, but for plantation rubbers which are homogeneous a sample of 10 lbs. is ample.

If the rubber is very hard it may be soaked (after weighing) for a few hours in warm water.

After the rubber is washed it should be dried in vacuum and weighed. Excessive washing in hot water must be avoided for at least two reasons. The rubber may become tacky and does not release the particles of debris; and, if vulcanization and mechanical tests are contemplated, false results may arise due to the deterioration of the rubber.

Fine Hard Parà shows about	16–18%	washing loss	
Plantation Smoked Sheet	1–1.3%	"	"
Plantation Pale Crêpe	0.5–1%	"	"
Sprayed Latex Crêpe (Hopkinson's Process)	8–9%	"	"

ANALYSIS OF RAW RUBBER

Chief Determinations.—Moisture, resin (acetone extract), insoluble, protein, ash, rubber, traces of coagulant.

Moisture.—Place 5 g. of rubber (cut into snippets with a pair of scissors) into a flat porcelain basin (tared) and dry the material in a vacuum oven for two hours at 60° C. (apply vacuum gradually); or in an ordinary air-oven heated to 80° C. for three hours or until weight is constant, or by desiccation in vacuo over concentrated H_2SO_4. This process is to be preferred.

The moisture may also be determined by difference after extraction with acetone (see next paragraph). Original weight of rubber *minus* the sum of the acetone extract and residue from extract gives the amount of moisture.

Resin (Acetone Extract).—Use a Soxhlet extractor or Cottle's (Underwriters) Apparatus. Take a 3–5 g. sample of the washed and dried rubber, cut up fine or rolled out into a thin strip.

If tacky or liable to coalesce, interleave the material with muslin or hard

filter paper. Charge the thimble with the sample and the tared flask with 60 ml. pure acetone (freshly distilled over anhydrous K_2CO_3, using the fraction 56°–57° C.).

If muslin is used to enclose and interleave the rubber it is well to fold over the lower end of the roll and fasten it by a few stitches so that there is no possibility of any of the snippets or detached particles working out between the folds.

Distil on water-bath or electric hot-plate for 8 hours. Detach the extraction flask, distil the solvent and dry the residue at 100° C. to constant weight.

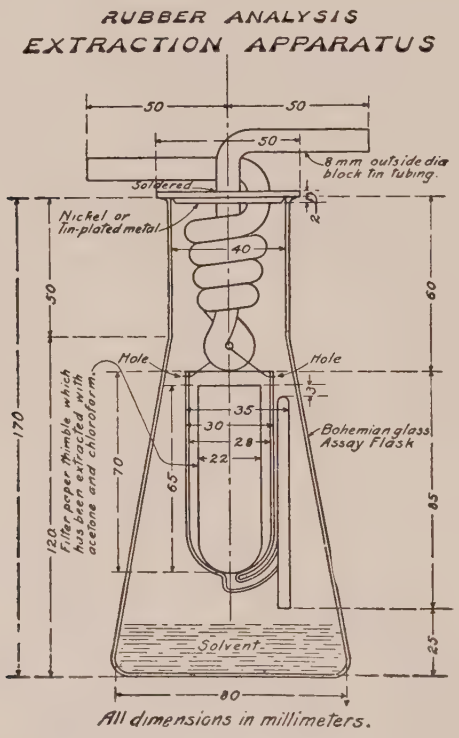


Fig. 285.

The flask should be inclined while drying in order to facilitate the removal of the solvent.

The increase in weight of the tared flask = acetone extract.

The residue can generally be easily detached from the muslin and can be weighed (as a check) after drying in vacuo over H_2SO_4.

Figure 285 shows the construction of Cottle's Extraction Apparatus (" Underwriters " design). The advantages of this extractor over the ordinary Soxhlet are (1) that it is compact, (2) the reflux condenser is immediately above the cup holding the sample, (3) the material being extracted is continuously

in the vapor of the solvent at its boiling point and thus does not become chilled. (A possible disadvantage is that the size of the sample is somewhat limited.) Only glass or metal joints should be used in any extraction apparatus (i.e., no cork, rubber, or other extractable substance should come into contact with the solvent).

It should be noted that both the extract and the acetone extracted rubber are liable to oxidation—therefore the drying should be carried out quickly at lowest convenient temperature. Any prolonged heating should be avoided. Weigh immediately.

Brown glass apparatus is sometimes recommended to eliminate the effect of light.

The percentage of "Resin" is generally characteristic of the brand—Parà (1.3%), Congo (4–6%), Kassai (4.5%), Borneo (10%), Ceylon Plantation (3.2%), Guayule (average 18%), Pontianak (80%). The character of the "Resins" is important, as, technically, rubber containing hard resin is preferred. Part of the acetone extract is saponifiable and part contains unsaturated compounds. (Iodine value of rubber "resins"—Parà 118, Borneo 31, Guayule 94.) All rubbers except Parà contain optically active "resins" and this fact has been proposed as a means of detecting rubber other than Parà in a mixture. The optical activity is always dextro-rotatory and it has been observed that the more optically active, the less saponifiable is the resin.

To Determine the Acid Value of the Acetone Extract.—Take up the weighed acetone extract with warm neutral ethyl alcohol. Titrate with N/10 alcoholic KOH, using phenolphthalein as indicator. Calculate the number of milligrams required to neutralize 100 g. of the original rubber (=acid number).

Ash.—Heat 3 g. of the sample in a porcelain crucible of about 40 ml. capacity. In an asbestos card, cut a hole of such a size that when the crucible is placed in it, the base of the crucible will protrude 1 cm. below the level of the asbestos. The crucible is placed on a tripod and heated gently at first with a small Bunsen flame until volatile material ceases to be evolved. During the initial stages of incineration, care must be exercised that the volatile decomposition-products do not inflame (or losses may occur rendering the results unreliable). Finally the temperature is raised to dull red-heat, and ignition is continued until all the carbon is burnt off. The mineral matter occurring in raw rubber varies with the source and mode of preparation. First quality Pale Crêpe ranges from 0.10% to 0.5% ash. The color of the ash should be noted. If white or pale yellow, and infusible, silica, lime and magnesia are possible constituents. If highly ferruginous the ash has a brick red color. Having now determined the moisture, "resin," ash, and washing loss, an approximate figure for the rubber hydrocarbon may be calculated by difference.

Determination of Copper in Crude Rubber

Ash a 20-g. sample over a Bunsen burner and finally in a muffle furnace. Do not expose to a higher temperature than a dull red heat. Particles of carbon enclosed by the ash need not be burned off as any portion of the copper existing as chlorides may be volatilized at the same time. Add 5 ml. of concentrated HCl and heat the crucible until acid boils. Transfer by means of a

fine stream of water and rubber policeman to a small beaker. Boil for a few minutes.

After the solution has cooled make it alkaline with NH_4OH. Heat on a steam plate until the volume of the solution is not more than 15 ml. (a steam plate is best for heating as there is often danger of spattering). By this time all of the excess ammonia will have been driven off. Add a few drops of bromine water and heat to boiling. (1) Filter immediately through a Gooch crucible into a graduated vessel (a graduated test tube which will slide inside the usual suction filter flask serves the purpose nicely). Dilute the solution to 30 ml.

Place 10 ml. of the solution, unless the copper is abnormally high (.01%) or low (.0005%), in a 50-ml. Nessler tube. If the copper concentration is high (.01%) use 5 ml. of solution, and if the copper concentration is low, use 20 ml. of solution. Add 22.5 ml. of 95% pure ethyl alcohol and 2.5 ml. of a 1% solution of sodium diethyldithiocarbamate in 95% pure ethyl alcohol. Mix thoroughly.

For a standard (2) prepare a similar solution in a Nessler tube using 10 ml. of water in place of the portion of the sample. Add a solution containing 0.00001 gm. copper per ml. from a pipette graduated in tenths ml. until an equivalent color is produced.

Calculation:

$$\frac{(\text{Ml. of Standard}) \times (\text{gm. of Cu per ml.}) \times 3}{\text{wt. of sample}} \times 100 = \%\ \text{Cu.}$$

(1) The bromine is added to precipitate the manganese as manganic hydroxide, manganous hydroxide being soluble in ammonium salts. Since as much as 0.000075 gm. of manganese has no effect on the indicator, the bromine treatment may be omitted if the amount of manganese in the rubber is known to be less than .001%.

(2) The standard Cu solution is made of $CuSO_4$ in a 5% NH_4OH solution, the strength of which is .00001 gm. Cu per ml. of solution. It is standardized by electrolysis method using Pt electrodes.

Determination of Manganese in Crude Rubber

Ash a 10 gm. sample in a large crucible. Start the ashing process on an open flame at about 200° C. slowly raising the temperature to 600° C., then place it in a muffle furnace at about 1200° C. until a white ash results. To the ash in the crucible add 35 ml. H_3PO_4, 35 ml. H_2SO_4 and 30 ml. HNO_3 and heat to near boiling until ash is dissolved. Cool and filter through asbestos and wash filter pad once with HNO_3 and then place filtrate in a 250-ml. beaker and heat on steam plate. Add a small amount (0.2 gm.) of sodium periodate and continue heating until constant color is present. Dilute with water to a definite volume (250–500 ml.). Compare this solution with a standard made up as follows: Dissolve 0.406 gm. of manganese sulfate ($MnSO_4$) in 1000 ml. of distilled water. 1 ml. of this solution is equal to .001 gm. manganese or .01%. This solution is used as a primary standard so great care should be exercised in its preparation.

Place 1 ml. of standard manganese sulfate solution in a small beaker (250 ml.) and add 35 ml. H_3PO_4, 35 ml. H_2SO_4 and 30 ml. HNO_3, heat almost to boiling (90° C.), and add 0.2 gm. of sodium periodate and continue heating until a constant color is present. Dilute with water to 100 ml. The standard is then ready for comparison with the solution of the unknown.

Place an aliquot of 25 ml. of the solution of the sample in a Nessler tube and then measure from a burette varying volumes of the standard $HMnO_4$ solution and place in other Nessler tubes and dilute with water to the mark. In this manner make a standard solution to match the color intensity of the sample.

Calculations:

$$\frac{(\text{ml. of standard}) \times (\text{gm. Mn per ml.}) \times (\text{aliquot portion})}{\text{wt. of sample}} \times 100 = \% \text{ Mn.}$$

The Organic 'Insoluble.'—(This material consists chiefly of protein-like substances.) There are various methods in use. Weigh out 25 g. of rubber and mix on rolls.

(*a*) Take 2 g. of the washed dried rubber in a flask. Add 10 ml. toluene and heat for 2 hours (under a reflux condenser) upon a sand bath. Allow to settle and filter, or better, centrifuge for half an hour. Pour off the supernatant liquid, add more toluene, mix and whirl again. The compact insoluble is received on a tared ashless filter.

Dry and weigh. Incinerate and weigh ash. The difference = organic insoluble (Caspari).

(*b*) Heat 1 gram of the finely divided sample with 10 ml. of phenetol for 5 hours. Dilute with benzene. Allow to settle, filter, rinse on to a tared dish, dry and weigh.[3]

(*c*) Warm 2 g. of rubber with 15 ml. petroleum (B.P. 200° C.) in a small flask for half an hour or until swollen. Dilute with 100 ml. benzene. Filter or centrifuge as in (*a*) (Caspari).

(*d*) Frank recommends that the sample be digested with cymene and centrifuged. When consolidated at the bottom of the tube it can be washed with benzene.

(*e*) Spence & Kratz dissolve the rubber in benzene to which they add 0.5% trichloracetic acid to lower the viscosity and thus allow the insoluble to settle out, when it may be washed with benzene, filtered and weighed.

(*f*) Tschirch and Schmidt heat the rubber at 80° C. with pentachlorethane and claim to obtain complete separation of the "insoluble."

Protein (Total Nitrogen).—Place 2 g. of the washed dried rubber in a 500 ml. Kjeldahl flask made of Pyrex or other heat-resisting glass, and add 30 ml. concentrated H_2SO_4 (or 20 ml. of concentrated H_2SO_4 and 10 ml. fuming sulfuric acid) together with 0.2 g. of mercury or mercuric oxide. Loosely stopper the flask with a small glass funnel, and heat at first on a sand bath and then over a naked flame gradually increasing the temperature to vigorous boiling until the liquid is light straw-colored and transparent.

This operation generally takes 2–3 hours.

Cool, and dilute with 200 ml. water.

[3] Beadle & Stevens, Analyst, **37**, 13 (1912).

The solution now contains all the nitrogen in the form of $(NH_4)_2SO_4$. Fit to the flask a distillation tube containing a "splash bulb." Measure into an Erlenmeyer flask 20 ml. $(N/10)\cdot H_2SO_4$, or more, according to the amount of N (NH_3, protein) present. Allow the end of the distillation-tube to dip beneath the surface of the standard acid. Detach the distillation-tube from the Kjeldahl flask and add 80 ml. NaOH (sp.gr. 1.35) cautiously down the side, keeping the solutions from mixing until later.

Add a solution containing 2 g. sodium sulfide in 20 ml. water, and then about 0.5 g. zinc in small pieces.

Now gently whirl the Kjeldahl flask, connect the tube and distil the ammonia into the standard $(N/10)\cdot H_2SO_4$.

When 100 ml. of the distillate has passed over, disconnect the tube and wash the end into the standard acid.

Titrate the excess of $(N/10)\cdot H_2SO_4$ with $(N/10)\cdot NaOH$ using methyl orange as indicator.

Calculate the nitrogen and multiply the value by 6.25 to obtain the weight of protein in the rubber. (The average N content of protein is 16.5%.

Wilfarth's modification of the Kjeldahl process is also recommended for the total N in rubber. It consists in digesting 1 g. of rubber with 30 g. concentrated H_2SO_4, 7 g. K_2SO_4 and 1 g. anhydrous copper sulfate for four hours and proceeding as usual.

A blank Kjeldahl should be run on the reagents used.

Instead of distilling the ammonia evolved by the NaOH into $N/10\cdot H_2SO_4$ as described above, the gas may be absorbed by cold distilled water and the amount determined by Nessler's reagent (See page 2049).

As stated previously, the protein material contained in rubber is capable of being separated from the nitrogen-free material by a solvent method (see under Organic Insoluble).

Parà rubber generally contains about 0.4% N, corresponding to a protein content of about 2.5%.

The amount of protein depends upon the source and mode of preparation of the rubber and may amount to 10% and over.

Determination of the Rubber Hydrocarbon.—As previously stated, for technical purposes it is sufficient to subtract the sum of the percentages of washing loss (moisture and dirt) ash, organic insoluble (protein) and acetone extract from 100 to obtain the percentage of rubber hydrocarbon. Such a method is far from ideal but up to the present no entirely satisfactory direct method of determining the rubber hydrocarbon has been evolved, and those suggested are generally somewhat tedious.

(*a*) ***Spence's Method.***—Take about 1 g. of the acetone extracted rubber (vacuum dried). Add 100 ml. cold benzene. Allow to swell, and make up to 200 ml. with benzene. Mix thoroughly and filter through a tube plugged with glass-wool (or allow to settle).

Take an aliquot part of the solution and evaporate to dryness in a current of CO_2. Weigh.

(*b*) ***Precipitation Method.***—Weigh out 3 g. of the material and swell it in 10 ml. of toluene. Make up to 100 ml. with toluene. Allow to settle (or centrifuge).

Take up in a pipette 50 ml. of the supernatant liquid and allow it to run into 100 ml. warm alcohol (95%), stirring meanwhile. Remove the clot by means of a glass rod to another dish, squeeze out, and redissolve in toluene (100 ml.).

Reprecipitate by alcohol. Squeeze out the alcohol and transfer the clot to a tared watch-glass. Dry to constant weight, preferably in vacuo. Calculate per cent of rubber.

If the rubber contains much resin, use the acetone extracted material.

(*c*) ***Fendler's Method.***—Take 1 g. of the washed dried material. Extract with acetone for 8 hours. Dry the sample. Dissolve the residue in petroleum ether and make up to 100 ml. with the solvent. Allow the " insoluble " to settle out. An aliquot part of the solution is taken and evaporated, drying subsequently in CO_2.

(*d*) ***Tetrabromide Method.***—(Budde's Method, Spence & Galletly's modification.) The value of this method is lessened by the fact that proteins and resins absorb bromine.

Weigh out 0.2 g. of the original rubber sample. Extract it with acetone for 8 hours. Place the residue in a wide-mouth bottle, cover it with 50 ml. carbon tetrachloride and allow it to swell overnight. (The brominating solution is made by dissolving 3 ml. bromine and 0.5 g. iodine in 500 ml. carbon-tetrachloride.)

Add 50 ml. of the " brominating solution " and allow the reaction to continue for six hours with occasional shaking. Add 50 ml. of absolute alcohol, with stirring. Allow to settle and filter. Wash with a mixture of alcohol and carbon-tetrachloride and finally with alcohol. Dry at low temperature and weigh precipitate. Ignite the precipitate. Difference in weights = Tetrabromide.

Assume the formula $C_{10}H_{16}Br_4$ (wt. $\times 0.298$ = rubber hydrocarbon), or the precipitate of tetrabromide may be fused in a platinum crucible with about 8 gr. of a mixture of Na_2CO_3 and K_2CO_3 (equal parts). Heat to clear fusion. Cool and leach with water. Acidify with HNO_3, and add enough $AgNO_3$ solution to precipitate the bromide. Heat gently to agglomerate the AgBr. Filter and determine weight of AgBr by any usual method. Calculate, 4 Br : $C_{10}H_{16}$: : amount of Br in AgBr : x.

The results obtained are often too high (substitution of Br takes place as well as addition, and the protein in the rubber also absorbs a little Br).

(*e*) ***Nitrosite Method*** (Alexander, Harries).—Dissolve 1 g. of the rubber (acetone extracted) in benzene. Pass nitrous fumes (obtained by the action of concentrated HNO_3 upon As_2O_3 (or starch)), through a drying tower containing P_2O_5, and thence through the rubber solution. The leading tube should be wide. Continue the current for one hour.

Allow to settle and decant through a weighed " Gooch," deposit the precipitate and wash with benzene. Pass the gas again through the filtrate and allow to stand overnight. Decant through the " Gooch," wash with benzene or petrol-ether and then with ordinary ether.

Dry at 75° C. and weigh.

The composition of the nitrosite is said to be $C_{10}H_{15}O_7N_3$.

Wesson and Knorr's Method (as modified by Tuttle and Yurow).—This is

claimed as the only nitrosite method yielding sufficiently exact results. Take 0.2–0.5 g. of rubber (dried).

Extract with acetone for 8 hours. Dissolve the residue in chloroform and pass the nitrogen-oxide gas until the solution is green. Allow the solution to stand overnight, and filter through a " Gooch " lined with asbestos. Evaporate the filtrate to dryness. Dissolve the residue in acetone and filter.

Take an aliquot part of the solution in a combustion boat and evaporate to dryness. The residue is ignited in a combustion tube and the products are led through a train of absorption bulbs (eight in all).

The first three contain a mixture of concentrated H_2SO_4 and $K_2Cr_2O_7$, the fourth contains zinc dust, the fifth is packed with soda-lime, the sixth with calcium chloride; the seventh bulb contains H_2SO_4 and $K_2Cr_2O_7$ while the eighth holds a dilute solution of palladium chloride.

The fifth, sixth, and seventh absorption bulbs are weighed before and after the combustion. The increases in weight give the total CO_2 and H_2O formed, from which the rubber content of the specimen is calculated.

(For details see *I. R. W.*, **57**, 17 (1917).)

ANALYSIS OF RUBBER SOLUTIONS

Determinations Required.—

1. Nature and amount of solvent.
2. Percentage of rubber.
3. Content of total solids.

The Solvent.—Take an adequate sample and separate the solvent by steam distillation. Separate the water and the solvent by means of a separatory funnel. Add a suitable dehydrating agent (i.e., fused calcium chloride) and allow the solvent to stand over this for a day.

A fractionation test should be undertaken and the nature of the solvent investigated.

To Determine the Proportion of Solids to Solvent.—Take a representative sample of 10 g. in a stoppered weighing bottle. Remove the stopper and place the bottle and stopper in a clean porcelain basin and evaporate the solvent in an electrically heated vacuum desiccator. The difference in weight = weight of solvent.

Investigation of the residue. Cut it into snippets and extract with acetone. The dried residue from acetone may be dissolved in acetic anhydride by Morawski's Method and examined for colophony by the Liebermann-Storch reaction (evanescent violet coloration with concentrated H_2SO_4).

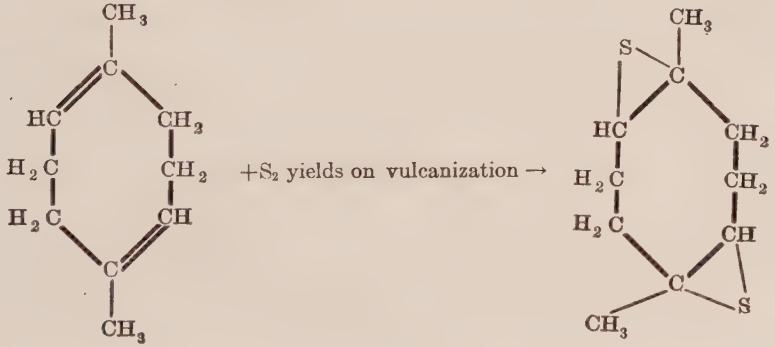
Inorganic fillers are determined as follows: Weigh the sample, dilute with petrol ether to such degree as will permit the inorganic fillers to settle. Filter or centrifuge. Wash the residue with the solvent. Dry and weigh.

ANALYSIS OF VULCANIZED RUBBER

The vulcanization of rubber is brought about by (1) heating with sulfur, (2) dipping into a dilute solution of sulfuromono-chloride in CS_2 (cold process for thin goods), (3) by exposure to the vapors of S_2Cl_2 (vapor cure), or (4) by the simultaneous action of hydrogen-sulfide and sulfur-dioxide (Peachey Process).

The properties of the resulting vulcanisates vary with the percentage of sulfur, the time of vulcanization and the temperature of the "cure"; also the nature of the additions to the mixture.

If the sulfur is limited to about 10% soft vulcanisates are produced. When the proportion of sulfur is raised (up to 32%) hard rubbers are formed. The change of the rubber hydrocarbon to hard-rubber (ebonite) may be represented *probably* by the following equation. (Although Wo. Ostwald is of opinion that the process of vulcanization is purely physical (adsorption) it is now generally accepted that the main action is one of chemical combination.) Vulcanized rubber is characterized by a great increase in resiliency, a lower temperature-coefficient of its elastic properties and a marked change in behavior towards solvents. The process of vulcanization is irreversible.



A representative sample must be obtained. Remove any extraneous material such as paint, lacquer, etc., by mechanical means. Powdered talc or starch should be removed by a brush or clean cloth. Bloom (powdered sulfur), waxes, etc., which have risen to the surface should be included in the sample. Metal (wire, studs) should be separated.

If the rubber itself is to be examined it should be freed from any applied fabric, but textile material actually forming part of the mixture should be included.

If the rubber consists of distinct layers of different composition, these should be worked up separately.

The sample having been isolated, it is cut up into snippets with scissors. Hard rubber (ebonite, vulcanite) is rasped with a coarse clean file and any iron filings introduced are removed by a magnet.

Unvulcanized doughs and reclaim may be rolled out into a thin sheet on the laboratory mill. The prepared bulk sample should be preserved in a stoppered wide-mouth bottle preferably of brown glass.

The scheme of analysis is that of Weber and Henriques, with modifications. It is rarely necessary to go through the whole scheme. The appearance of the sample will give valuable information. If the rubber is light or red in color it is obvious that carbon black, pitch, tar, bitumen, and Pb compounds are absent. In this case, the chloroform-extraction can be omitted.

Moisture.—Take a 2 g. sample and dry it to constant weight in a vacuum-desiccator containing concentrated H_2SO_4. Loss of weight = Moisture. (If the rubber contains no material likely to be melted out, the sample may be dried in an air oven at 80° C. or in an electrically-heated vacuum-desiccator.)

Water-Soluble Constituents.—Take a 10 g. sample in a 300-ml. flask and add 100 ml. H_2O. Heat to 80° C. and allow the specimen to soak for a few hours. If present, the following substances will be found in the solution:

Starch (dextrin), gelatine (glue), some accelerators (aniline), and part of the inorganic fillers (lime, $CaSO_4$).

Test for alkali; starch by iodine; size (gelatine) by Tannin. Aniline may be detected by the violet coloration with hypochlorites. Glycerin may be detected by evaporating a portion of the solution to dryness and heating the residue with $KHSO_4$ when the odor of acrolein is obtained.

For other constituents proceed as follows: Take a 2 g. sample and extract with pure acetone, for 8 hours.

A. Solution	*B.* Residue. Extract with alcoholic KOH (1N)	
	C. Solution contains Sulfurized substitutes Chloro-sulfur substitutes Oxidized (brown) oils Polymerized oils (Sulfur and chlorine in above)	*D.* Residue contains Rubber Hydrocarbon Mineral fillers (Sulfur of vulcanization) (Chlorine of vulcanization)

Note.—The mineral fillers are determined on a part of Residue *D* by ignition, and the rubber-hydrocarbon is calculated by difference. The Residue *D* is also used to find the sulfur and chlorine of vulcanization by method given on pages 1985–1986.

Full Scheme for Analysis of Vulcanized Rubber.—If the rubber is black it may contain one or more of the following substances: Carbon black, pitch, tar, bitumen, Pb compounds. For a systematic investigation, the following procedure may be followed: (This scheme is based on the work of Weber, Henriques and others.)

Take a 5 g. sample and extract with Acetone for 8 hours. (Hard rubber requires 48 hours.)

A. Extract may contain:

1. "Resins" of Rubber.
2. Added resins.
3. Mineral Oils.
4. Waxes.
5. Fatty Oils.
6. Resin Oils.
7. Free Sulfur.
8. M.R. (part).
9. Cellulose-Esters.
10. Naphthalene, aniline.
11. Accelerators.
12. Antioxidants.
13. Certain organic colors.

(See page 1980)

B. Residue.—Extract for 4 hrs. with chloroform (immediately, without drying)
(See page 2002)

C. Extract may contain:

1. Pitch.
2. Bitumen.
3. Tar.
4. Sulfur in the above.
5. M.R. (part).

(See page 1982)

D. Residue.—Extract with N Alcoholic KOH.
(See page 1982)

E. Extract may contain:

1. Sulfur Sub.
2. Chloro-Sub.
3. Oxidized Oils.
4. Sulfur and Cl in the above.

(See page 1982)

F. Residue.—Weigh and extract with a rubber solvent. (Petrol, xylene, etc.)

G. Extract may contain:

1. Rubber hydrocarbon.
2. Sulfur and Cl in above.

(See page 1982)

H. Residue.—Weigh and extract with boiling water.
(Wt. of *F* − Wt. of *H* = *G*.)

I. Extract may contain:

1. Starch.
2. Dextrine.
3. Gelatine.
4. Albumen.

(See page 1978)

K. Residue may contain:

1. Minerals.
2. Free Carbon.
3. Vegetable fibre.
4. Sulfur in minerals.

(See page 1988)

Note.—The time required for the Acetone Extraction (and its completeness) depend upon the apparatus and the speed of siphoning; also upon the rubber and its subdivision. The siphon should function once in about three minutes.

Inspection of Acetone Extract.—Evaporate the solvent and dry at 90° C. Note color and viscosity—If pale and transparent and small in quantity, absence of gross additions may be inferred. Fluorescence indicates the presence of mineral-oil. Test for rosin (colophony) and rosin oil by the Liebermann-Storch reaction.

Solid Waxes.—Warm a little of the acetone extract with absolute alcohol. Cool. Waxes deposit.

Detailed Examination of the Acetone Extract

Total Sulfur.—(All reagents used must be free from sulfur.) Dry the acetone extract and weigh. Take an aliquot part in an Erlenmeyer flask, add 1 g. of MgO and 10 ml. of concentrated HNO_3 and 1 ml. bromine.[4]

Allow to stand for a few hours. Start heating on a steam bath,—increase temperature on sand bath. Add more reagent if required. When oxidation is complete, transfer to a porcelain dish and evaporate dry on a steam bath. Add 5 ml. concentrated HCl and evaporate dry; bake gently; repeat this operation. Add concentrated HCl and transfer to a flask by means of hot water. The sulfur is now in solution as sulfate. Filter hot. Make up to 100 ml. with hot water. Heat to nearly boiling and add 10% $BaCl_2$ solution. Allow to stand overnight.

Filter the $BaSO_4$. Wash with hot water, ignite in porcelain crucible to constant weight. Calculate S.

Saponifiable and Unsaponifiable Matter.—Take an aliquot part of the dried extract (½ g.), add 25 ml. N/2 KOH, and heat under a reflux condenser for two hours. Transfer to a separatory funnel. Cool to room temperature. Add 20 ml. ether and shake carefully. Separate the two layers, and wash the ether layer several times with cold water until the water no longer has an alkaline reaction. Transfer the ether extract to a tared flask and evaporate the ether. Dry to constant weight at 80° C. (=unsaponifiable).

The aqueous alkaline solution from the ether extraction is now acidified with dilute H_2SO_4 to set free the fatty acids, from the soaps.

Transfer to a separatory funnel. Shake out with ether as before and repeat. Collect the ether fractions in a clean separatory funnel and wash free from acid by repeated shaking with cold water.

Transfer the ether solution of fatty acids to a tared flask, evaporate and weigh, (=saponifiable matter, chiefly resins and fatty acids).

If the rubber should contain cellulose-esters they will be dissolved by the acetone and will cause the acid aqueous liquid to be strongly turbid, and if suspected the fluid is neutralized by ammonia and evaporated to a paste, heated with 10 ml. " cuprammonium solution " and allowed to stand for 12 hrs. in a covered vessel, shaking periodically.

The cellulose will dissolve and a clear solution will be obtained. Acidify with HCl. Prepare a Gooch lined with asbestos. Filter, wash, dry, and weigh the cellulose. (For separate determination of cellulose see page 1987.)

The Unsaponifiable Matter in the Acetone Extract May Contain:

1. Substances occurring in the original rubber.
2. Mineral oils.
3. Solid paraffin-hydrocarbons (paraffin-wax, ceresin, etc.).
4. Tar and asphalt.
5. Wax alcohols.

Take a known quantity of the unsaponifiable matter and extract it with hot absolute alcohol. The residue consists of tar and asphalt. Evaporate the

[4] If certain modern accelerators have been used a bromine-nitric acid oxidation, followed by perchloric acid, is a more effective oxidizing treatment ("Captor," etc.).

alcoholic solution to 50 ml. Cool the flask and then place it in a freezing mixture capable of producing a temperature of *minus* 5° C. The solid paraffins will separate out. Filter through an iced funnel and wash with ice-cold alcohol. Remove the funnel from the ice-pack and dissolve the residue through the filter with hot chloroform into a tared flask. Evaporate the solvent and dry to constant weight (=solid paraffins).

The alcoholic solution remaining after freezing out the solid paraffins is evaporated to dryness on a water-bath. Dissolve the residue in CCl_4 (15 ml.) and transfer the solution to a separatory funnel. Add 15 ml. concentrated H_2SO_4 to the funnel and shake carefully. Separate and repeat till the H_2SO_4 extracts no more colour.

Draw off the acid. To the CCl_4 solution add distilled water and then enough ether to dilute the CCl_4 to make it float above the water. Shake and repeat the washing until the " CCl_4-ether solution " is acid-free. Transfer the " CCl_4-ether solution " to a tared flask and evaporate. Dry constant at 90° C. This gives the weight of the liquid paraffins, and mineral oils.

The Saponifiable Matter in the Acetone Extract comprises:

Fatty acids.
Resin acids.
Added Resins (e.g. Colophony).

Take the aqueous portion from the separation of " Saponifiable " and " Unsaponifiable." Acidify with HCl. Shake with ether. Wash the ether free from acid. Filter the ether solution and wash with the solvent. Distil the ether and dry the residue for one hour at 95° C. This gives the weight of the fatty acids, obtained from the saponifiable oils.

To determine resin (colophony) use Parry's Method:

Take part of the original acetone-extract or the saponifiable above. Dissolve in 20 ml. of 95% alcohol. Add dilute NaOH (made up with 1 of alcohol +2 of H_2O) until just pink to phenolphthalein. Heat for 10 minutes. Cool. Transfer to a 100-ml. graduated stoppered cylinder. Fill to the mark with ether, and add 2 g. $AgNO_3$. Shake and allow to settle. Silver salts of abietic acid and other organic acids form. The silver salts of the free fatty acids are insoluble in ether, but those from colophony (abietic acid) give silver salts which are soluble. Therefore take 50 ml. of the clear solution in a separatory funnel and shake with 20 ml. dilute HCl. Draw off the ether layer by means of a pipette and shake twice with ether. Unite ethers and wash. Distil the ether solution in a tared flask. Residue = Colophony. Dry at 105° C. and weigh ($\times$ by 2).

The Detection and Determination of Accelerators is very difficult and generally impossible owing to the complex nature of the accelerators themselves, the small amounts used, and to the great changes they undergo during vulcanization.

Some disappear altogether (i.e. isopropyl-xanthates).

Evidence of the use of organic accelerators may be inferred by the enhanced mechanical properties, the sub-normal sulfur content, and low vulcanization coefficient. For further information see Twiss and Martin (Gummi Zeitung. **35**, 1151 (1921)).

Examination of the Chloroform Extract

Evaporate the extract on a steam bath. Dry to constant weight in an air-oven at 95° C. If the extract is fluorescent, or of color darker than yellow, bitumen is present. Part of the asphalt and tar may also be found here.

Dissolve the dry extract in benzene (warm). Allow to stand for 12 hrs. Filter, wash several times with benzene.

The substances insoluble in benzene are called " Hard Asphalt." It should be borne in mind that soft vulcanized rubber always yields about 1% to chloroform. Sometimes it is soluble to the extent of 2%.

If the figure 1% is exceeded and bituminous bodies are shown to be absent (light color of extract) it is certain that the rubber has dissolved in excessive amount. (This indicates (1) that the material is undercured, or (2) contains " reclaim," or (3) has been deteriorated in manufacture by excessive milling, or (4) that the rubber has undergone excessive ageing.)

If the extract is brown, asphalts or " M.R." are present.

Asphaltum is much used in cable coverings to remove microporosity, and to increase insulation.

The Alcoholic KOH Extraction

This reagent removes the main part of the fatty oils, the white and brown " factis " (oil-substitutes). It also dissolves a portion of the natural albumin (casein, and wool if present). If phenol-resins are present they will also be affected.

The residue from the chloroform is dried at 50° C. and transferred to a 200 ml. flask. Add 50 ml. benzene and allow it to stand 12 hours. Add 50 ml. N alcoholic KOH and boil under a reflux condenser for 4 hours. Filter and wash. Grind the residue in a mortar, leach with hot absolute alcohol, and finally with hot water. The washings are combined with the filtrate and evaporated dry. Add H_2O, and transfer to separatory funnel. Acidify with dilute H_2SO_4.

Allow to cool, add ether, and shake. Separate the ether and aqueous layers, and repeat. Combine the ether fractions in another funnel and wash with cold water till acid-free. Add the " waters " to the aqueous fraction. Evaporate the ether in a tared flask to constant weight. Calculate per cent of residue (= weight of fatty acids). " Total unsaponifiable " minus the sum of solid and liquid hydrocarbons gives the unsaponifiable resinous matter.

The Determinations of Sulfur and Nitrogen in the Alcoholic KOH Extract are made by the same methods as described for sulfur in acetone extract.

Determination of Total Fillers.—Incineration of the original rubber in an open crucible (as described under Ash, page 1971) forms the simplest method, but this method fails if any of the fillers are decomposed with loss of volatile matter (i.e. HgS, $CaCO_3$, free carbon, cellulose, etc.). HgS is completely volatilized, carbonates evolve CO_2, and sulfides change to oxides.

Take 1 g. of rubber. Extract with acetone, and chloroform as usual. Dry the residue and transfer it to a 200-ml. flask (tared).

Add 25 ml. petroleum (B.P. 230° C.). Heat under a reflux condenser, until the rubber is in solution. Cool the flask and nearly fill it with benzene.

Allow it to stand until the fillers have settled. Decant and filter through a Gooch. Wash with hot benzene, alcohol and ether. Dry the crucible at 90° C. to constant weight.

A centrifuge will save much time.

If an autoclave is available the sample may be heated with xylol under pressure.

Determination of Sulfur

The sulfur in rubber may occur in various forms. The determinations usually required are total sulfur, free sulfur, sulfur of vulcanization, sulfur combined in the fillers (organic and inorganic).

During the analysis sulfur appears in the various extracts and residues.

1. **Total Sulfur (J. Rothe's Method).**—Take 1 g. of the rubber under test in a round-bottom Pyrex flask. Add 30 ml. concentrated HNO_3 and 1 g. MgO. Heat upon a steam-bath until fully oxidized. Heat more strongly upon a sand-bath to expel brown fumes.[5] (If carbon should remain repeat the oxidation with HNO_3 and heat again.) Add 5 ml. HNO_3 and dilute with 30 ml. H_2O. Filter and reserve the residue.

Filtrate.—Evaporate to dryness in a porcelain dish and bake the residue for 2 hours at 135° C. Moisten with HNO_3. Add H_2O and evaporate dry. Add 5 ml. concentrated HCl. Heat and dilute to 100 ml. with H_2O. Filter and wash residue. Boil the filtrate and add 10% $BaCl_2$ solution. Allow to stand overnight. Filter off the $BaSO_4$, and wash with distilled water. Dry, incinerate and weigh. ($BaSO_4 \times 0.1373 = S$.)

Residue (above).—Fuse in a crucible with about 5 g. of a mixture of Na_2CO_3 and K_2CO_3 (equal parts). When clear, allow to cool, leach out with hot water and boil the liquid. Filter.

Filtrate.—Acidify with HNO_3. Evaporate to dryness, bake at 135° C. for 2 hours. Add concentrated HCl. Heat and dilute with H_2O. Filter off any silica or antimony oxide.

Evaporate the filtrate to dryness, add concentrated HCl and evaporate again. Add dilute HCl and boil; filter. Add 10% $BaCl_2$ and calculate sulfur as stated above.

(Steven's Method, Analyst, 43, 1918)

0.5 g. of the rubber sample is digested with 20 ml. HNO_3 (1.42). Add 0.5 g. $KClO_3$.

Boil for 3 hours under a reflux condenser. Evaporate dry in a porcelain basin with the addition of 3 g. of magnesium nitrate. Heat cautiously over a naked flame. (The Mg salt moderates the combustion.) Any unburnt carbon is destroyed by digestion with HNO_3 and $KClO_3$. Expel excess of acid. Add 10 ml. HCl (concentrated) and cover the dish with a clock-glass. Gently heat until the red fumes cease to be evolved. Dilute the liquid, filter, and make up to 300 ml. Heat to boiling point and precipitate $BaSO_4$ with 10% $BaCl_2$. Allow to stand overnight. Filter and weigh.

[5] See note on page 907.

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(Kay and Sharp's Method)

This rapid method is carried out as follows:

0.25–0.5 g. of the finely divided sample is intimately mixed with 5 parts by weight of pure ZnO and 4 parts of KNO_3 in a porcelain crucible and a thin layer of ZnO as a cover. Put the lid on the crucible and heat gently until the reaction commences; then remove the flame for a time. Subsequently heat with the full flame for five minutes. Cool. Dissolve the contents of the crucible in dilute HCl and precipitate the sulfur as $BaSO_4$ as usual.

Bromine-Nitric Acid Method.—Method of Waters & Tuttle (Ind. Eng. Chem., 3, 734 (1911)). Take a 0.5 g. sample in a large porcelain crucible. Add 15 ml. of concentrated HNO_3 saturated with bromine. Cover the crucible and allow to stand for 1 hour. Heat for one hour on the steam bath. Remove the cover, rinse, and evaporate dry. Add 3 ml. concentrated HNO_3. Cover, warm for 15 minutes. Allow to cool and add 5 g. Na_2CO_3 in small portions down the side, and replace cover. Stir. Dry on steam bath and spread the mixture on the sides of crucible. Fuse and destroy all carbonaceous matter. Cool the melt and place the crucible and its contents in a 400-ml. beaker. Cover with 125 ml. H_2O. Digest for 2 hours. Filter. Wash the residue. To the filtrate add a few mls. of concentrated HCl. Cover and heat. Precipitate the $BaSO_4$ as usual. (Factor for sulfur = 0.1373.) The above methods do not distinguish between free sulfur, sulfur combined with the rubber hydrocarbon (sulfur of vulcanization) and sulfur in the fillers.

If barytes ($BaSO_4$) is the only sulfur-bearing filler, the zinc oxide-nitric acid method is correct.

Zinc Oxide-Nitric Acid Method for Total Sulfur (excluding sulfur in barytes).—Take a 0.5 g. sample in 500-ml. Erlenmeyer flask. Add 10 ml. ZnO-HNO_3 mixture made by adding 20 g. ZnO to 100 ml. concentrated HNO_3. Allow the "test" to stand at room temperature for about 12 hours. Add 15 ml. fuming HNO_3. Do not allow ignition to occur (cool if necessary). When a solution is obtained add 5 ml. saturated bromine water. Evaporate on a steam-bath to a syrup. If necessary add more of the reagents. Cool and add $KClO_3$. Evaporate dry. Heat more strongly until all the nitrates are decomposed.

Cool. Heat with 50 ml. concentrated HCl. (Any Ba salts are precipitated here.) Filter and dilute to 300 ml. Boil and precipitate with 10% $BaCl_2$. Calculate S.

In the presence of other sulfur-bearing mineral fillers, the solution-method for separating fillers from non-fillers is employed in conjunction with the bromine-nitric acid method, as follows: Take a 0.5 g. sample. Extract with acetone. Heat to 135° C. (until dissolved) with 25 ml. cymene in a 150-ml. flask.

Dilute to 100 ml. with petrol-ether. Allow to stand overnight. Filter through a "Gooch" with slight suction. Retain the residue in the flask, wash with 10 ml. portions of petroleum-ether, then hot benzene and finally with acetone. Again treat with the brominating solution. Evaporate dry. Add concentrated HCl and evaporate, and again HCl. Add hot water, filter and precipitate the sulfur in the filtrate by 10% $BaCl_2$ solution.

If $BaSO_4$ is present, make a fusion and subtract the sulfur in the mineral fillers from the total sulfur.

Sulfide Sulfur. Steven's Method (Chem. Analyst, **40**, 275 (1915)).—Arrange a Kipp Apparatus for CO_2; and a 250-ml. flask with an inlet tube reaching nearly to the bottom; a ground-in stopper should be used. The outlet tube from the flask is connected to two absorption bulbs containing lead-acetate solution.

Place in the flask 10 ml. concentrated HCl and then 20 ml. ether. Pass a current of CO_2 through the apparatus until all the air is displaced. Lift the stopper, and add 1 g. of the powdered sample. Again pass CO_2 (for 30 minutes), shaking occasionally. The H_2S evolved from the sulfides is absorbed by the lead-acetate. Heat the generating flask to ensure complete decomposition. Determine the lead-sulfide in the bulbs and calculate to sulfur. If pure nitrogen is available for sweeping out the apparatus, the procedure may be simplified by using NaOH in the absorption bulbs in place of lead-acetate. In this case, the sodium sulfide formed is oxidized to Na_2SO_4 by means of bromine. Determine $BaSO_4$ and calculate to S.

Sulfate-Sulfur.—Ignite a 1 g. rubber sample in a porcelain boat in a stream of CO_2. Boil the residue with Na_2CO_3 solution. Filter, acidify the filtrate with HCl, and boil to expel SO_2 from the sulfites. Precipitate the sulfate as usual with 10% $BaCl_2$. Calculate S.

Sulfite-Sulfur.—Proceed as described above for sulfate-sulfur except that instead of boiling off the SO_2, it is oxidized by bromine and thus converted to sulfate.

Precipitate the total sulfate by 10% $BaCl_2$ solution and calculate S. Subtract "*sulfur as sulfate*" from the "*sulfur as sulfite+sulfate.*" Difference = "sulfur as sulfite." Or the SO_2 boiled off may be absorbed in NaOH solution, oxidized, and precipitated as $BaSO_4$.

The Sulfur of Vulvanization can now be calculated. Subtract the various "sulfurs" determined from the total sulfur—the remainder = vulcanization sulfur, i.e., the sulfur actually combined with the rubber-hydrocarbon.

If the rubber is a simple "rubber+sulfur" mixture, the calculation of the sulfur of vulcanization involves the determination of the total sulfur by one of the methods described and the determination of the free sulfur (sulfur in the acetone extract). Subtract the latter from the former.

If the sample is a complicated mixture it is necessary to carry out the following extractions in accordance with Weber's scheme of analysis. Take a 2 g. sample and extract with acetone, chloroform, and alcoholic KOH. This leaves a residue containing rubber and fillers. Divide this residue into two parts; on one part find the Total Sulfur; on the other part carry out the solvent separation of the fillers and determine the sulfur in the latter by a fusion method.

The difference between these values will give the sulfur combined with the rubber-hydrocarbon.

The sulfur of vulcanization can also be obtained when the nitrosite method for determining the rubber is used. The nitrosite contains all the sulfur that was originally chemically combined with the rubber-hydrocarbon.

Take an aliquot portion of the acetone-solution of the nitrosite compound. Remove the acetone by evaporation and determine the sulfur in the residue

by the method of Waters and Tuttle ($Br-HNO_3$), followed by fusion with alkali and KNO_3.

The best way of arriving at the sulfur of vulcanization is the following:

Add together the free sulfur (the acetone extract), the sulfur found in the alcoholic KOH extract, and the sulfur in the inorganic fillers. Subtract the sum from the total sulfur found by the method of Waters and Tuttle.

Determination of Selenium (Method of E. H. Shaw & E. E. Reid).—Take 1 g. of the original rubber sample. Mix in a crucible with 0.5 sugar, 0.2 g. $NaNO_3$ and 14 g. Na_2O_2. Cover with a layer of Na_2O_2. Fuse gently. Cool, and leach out with H_2O. Boil until the H_2O_2 is decomposed. Filter. Acidify with HCl.

The selenium has been oxidized to selenic acid. Add concentrated HCl and cover with a watch glass. Boil. Allow to cool to 90° C. Pass a current of SO_2 gas (from the siphon) until the red precipitate (Se) has agglomerated, leaving the mother liquid quite clear. Rinse the watch glass and dilute with H_2O. Filter through a prepared "Gooch." Any selenium adhering to the sides of the beaker can be removed by alcohol. Wash the precipitate in the "Gooch," first with alcohol, then with H_2O. Dry at 115° C. to constant weight.

Determination of Chlorine (in cold vulcanization goods or mixtures containing white oil-substitute).—**(Henriques' Method.)** Take 1 g. of the original sample in a porcelain crucible and mix with 2.5 g. Na_2CO_3 and 2.5 g. KNO_3. (These reagents should be examined for chlorine.) Fuse gently and leach out with hot water. Heat nearly to boiling and filter. Acidify the filtrate with HNO_3. Determine the Cl gravimetrically or by the following method. Add 25 ml. N/10 $AgNO_3$ standard solution. Heat to 80° C. and determine the excess of $AgNO_3$ by means of standard N/10 NH_4CNS standard solution, using ferric-alum as indicator. (See page 271.)

(Carius' Method)

Place 0.3 g. of original rubber in a Carius Tube and add 5 ml. fuming HNO_3 and 1 g. of solid $AgNO_3$. Seal and heat in the furnace. Open the tube and empty contents into a beaker.

The residue consists of a mixture of AgCl and insoluble mineral matter. (Most rubber compounds contain mineral matter insoluble in HNO_3.) Heat the residue with dilute H_2SO_4 in a Pt crucible and add a few pieces of pure zinc. Allow the reaction to continue until the zinc has dissolved. Stir occasionally. Filter and wash with hot water. The silver has been reduced by the Zn and the chlorine is in the filtrate. Determine chlorine by the usual methods. (See page 265.)

Qualitative Test for Glue (Epstein & Lange's Method).—Take 3 g. of the rubber sample and heat with pure cresol for 16 hours at 120° C. The rubber dissolves. Cool and dilute with petroleum-ether. The glue and other insolubles settle out. Allow to stand overnight. Or the liquid may be centrifuged. Filter on a prepared "Gooch," wash with warm petroleum-ether, and then with hot benzene. Dry the crucible and contents at 90° C. Remove the contents of the crucible to a beaker and boil with H_2O. Filter and add a solution of tannic acid.

Quantitative.—The method of Epstein & Lange may be applied quantitatively.

Determination of Glue.—This may be calculated **approximately** from the N content of the original material after allowing for the natural protein of the rubber itself. The per cent N in rubber varies from 0.2 to 0.6. Some knowledge of the source of the rubber is necessary. But if the rubber contains accelerators or antioxidants, which is likely in modern practice, this method would give erroneous results unless the rubber is first extracted with acetone for eight hours. In any event the method involves a knowledge of the percentage of rubber in the sample and it is known that some of the N compounds natural to rubber are removed by acetone.

The Kjeldahl Method is as follows: Extract 2 g. of the original rubber with acetone for 8 hours. Determine the total N content as usual (running a blank on the reagents, and using the factor 6.25).

Assume the N in the rubber to be 0.4%. Subtract this from the total N and multiply the difference by 6.25.

The N in accelerators is variable; it may run as high as 20%, but is often less; only about 1% of accelerator is used in a rubber compound. Therefore an **approximate** idea of the amount of glue is possible.

Bone-glue is detected by testing the ash for phosphates. A high content of P. indicates bone-glue.

Determination of Cellulose

Cellulose may be present in two forms.

1. As the cotton fabric upon which the rubber was spread.
2. As a filler ingredient, in fiber form or cotton watse, etc.

To determine the relation of the tissue to the rubber material and to ascertain the structure of the fabric as well as the weight of rubber per unit area, a process is used similar to the solution method for Total Inorganic Fillers (or loading).

Take a convenient sample. If it has a thick coating of rubber, the latter should be removed as far as possible without damaging the fabric; reserve the rubber. Cut up the remainder of the sample into small pieces and heat in a flask (use reflux) with petroleum or in an autoclave with benzene or xylene. Continue the digestion until the rubber dissolves. Filter off the residue, wash with benzene and afterwards with ether. Dry and weigh.

The material still contains the loading between the fibers.

Heat with NaOH solution. Wash with H_2O. Heat with acetic acid and wash with water. Dry to constant weight at 100° C. Weigh.

Burn off the cellulose material and weigh again.

Loss of weight = cellulose (anhydrous).

As cellulose matter in the air-dry condition generally contains 7% moisture add 8% to the result to obtain the weight of the cellulose material as originally used.

This method of course fails if there are other combustible materials and volatile inorganic fillers.

Epstein & Moore's Method [6] (B. of S. Tech. Paper No. 154).—Take 0.5 g.

[6] See also Standard Methods, page 2009.

of the sample in a flask and add 25 ml. freshly distilled cresol; heat for four hours at 165° C. under reflux. Cool and add 200 ml. petrol ether, shake continuously for a time and then allow to settle. Decant the clear portion through a tared " Gooch." Wash the residue in the flask with hot benzene and then with acetone. Add hot 10% HCl to the residue in the flask and transfer it to the " Gooch." Wash with 10% HCl. Wash thoroughly with boiling H_2O (until free from chloride) and then with acetone until the filtrate comes through clear and colorless. Transfer to a tared weighing bottle. Dry at 105° C. to constant weight ($=A$). (This gives the weight of the asbestos pad+inorganic fillers and cellulose.)

(*a*) Transfer the contents of the weighing bottle to a flask and add 15 ml. acetic anhydride and 0.5 ml. concentrated H_2SO_4. Digest in the steam bath for 1 hour. Cool, and add 25 ml. 90% acetic acid. Filter through a tared " Gooch." Wash with acetic acid and afterwards with acetone. Dry the crucible at 105° C. Cool and weigh ($=B$). Loss of weight ($A-B$) = cellulose.

(*b*) Or the following procedure.

Transfer the contents of the weighing bottle (at A) to a flask and add 25 ml. of " Cu-Oxam" solution. Allow the mixture to stand for 12 hours, shaking at intervals. Filter through a tared " Gooch." Wash first with " Cu-Oxam," and then with dilute ammonia until the filtrate runs colorless. Dry the crucible to constant weight ($=B$). Net weight of the residue $A-$net weight of the residue $B=C$ (wt. of cellulose dissolved by the " Cu-Oxam.")

The weight of the cellulose may be confirmed by precipitating the cellulose from the blue filtrate by adding sodium chloride and then dilute sulfuric acid.

The precipitated cellulose is filtered, washed with hot H_2O until free from chlorides (test washings with $AgNO_3$). Dry the cellulose at 105° C. and weigh.

Determination of the Inorganic Fillers

Modern rubber practice makes use of a formidable list of inorganic fillers, in fact it is difficult to mention any low-priced material that has not been tried in rubber mixes.

The following list comprises substances that have proved of definite use and that may be found in rubber material at the present time. Some of these substances are used for specific effects (such as, aids to vulcanization, increase of tensile strength) whereas others are mere diluents added to cheapen the product.

All the inorganic fillers are added in finely powdered form. The most commonly used are: Zinc-oxide, litharge, lithopone, pumice powder, chalk, lime, clay, barium sulfate, magnesia, basic magnesium carbonate, pentasulfide of antimony.

The following are less common: Mercury-sulfide, arsenicals, red lead, white lead (basic lead-carbonate), lead-sulfide, ultramarine, lead-sulfate, zinc dust, ferric-oxide, aluminium-oxide, kaolin, calcium-sulfate, powdered glass, silica, asbestos, talc.

Before a systematic examination of the inorganic fillers can be made the organic material must be carefully removed. The inorganic constituents may then be determined in accordance with systematic inorganic analysis but the

following will give the general procedure in a rubber laboratory. For the purpose of separating the fillers, Rothe's Method is recommended, as this obviates the loss by volatilization of certain ingredients if present (As, Sb, Hg). (A rough idea of the amount of ash may be obtained by simple ignition in a tared porcelain crucible, and this should be carried out as a preliminary.)

For Rothe's Method the amount of rubber taken should be enough to produce 1 g. of ash. The weighed rubber is placed in a round-bottom Pyrex flask of about 300 ml. capacity. Add (per gram of rubber) 15 ml. concentrated HNO_3 and 2 ml. concentrated H_2SO_4. Heat on a sand bath for 1 hour and then more strongly to fumes of SO_3. Finally heat by naked flame to boil the H_2SO_4. Cool, and add more HNO_3 (10 ml.).

Heat until the liquid becomes colorless. If necessary add more HNO_3. Cool, and pour the strong acid solution into 50 ml. H_2O. Boil the solution, and filter.

The **residue** (*A*) may contain $PbSO_4$, $CaSO_4$, $BaSO_4$, silica, silicates, and (if Sb is present) antimony oxide and Pb antimoniate, stannic oxide. **Pb** may be removed by boiling the residue with several portions of ammonium acetate ($+NH_4OH$) solution or the hot ammonium acetate may be passed through the filter containing the residue. This leaching should be continued until the " washings " fail to contain Pb (test with K_2CrO_4 or H_2S).

Wash the **residue** and reserve it for further treatment (see under Ba). The " ammonium acetate-Pb solution " may contain a little calcium. The calcium in the filtrate from Pb is evaporated to dryness in a porcelain dish. The ammonium salts are ignited, the residue is dissolved in dilute HCl and Ca is determined (as on page 210).

Barium.—Take the residue after the removal of the $PbSO_4$ by ammonium-acetate (above). Ignite with a mixture of sulfur and Na_2CO_3 (equal parts). Apply one bunsen to the bottom and another to the top of the crucible and continue the heating until sulfur ceases to burn beneath the cover. Cool. Leach out with H_2O. Filter. The residue may contain $BaCO_3$ (silica and silicates) and PbS. The filtrate may contain antimony and tin (if present)—reserve (*B*). Take the residue, add hot HCl to dissolve the Ba, Ca, and Pb, leaving (as insoluble) the silica and silicates. [This insoluble should be ignited and fused with a mixture of $K_2CO_3+Na_2CO_3$. Leach with water and filter. (If any residue occurs here it should be tested for bases.) The filtrate from the alkali-fusion may be discarded as silica is best determined in a separate portion of the original sample.]

The acid filtrate containing the Ba and Ca is now tested for Pb and, if found, H_2S is passed through the solution to completely remove it. The Ba and the Ca are determined in the filtrate by usual methods (see page 122).

The **filtrate from residue A** may contain Hg, As, Sb, Sn, Zn, Cr, Fe, Ca, and alkali metals, etc.

Hg.—Pass H_2S to precipitate Sb, As, Sn, Hg. Filter and transfer with H_2S to a beaker. (Reserve, filtrate *D*.) Boil with dilute NaOH—the Sb, Sn, As dissolve—and filter the insoluble HgS. Wash the HgS and dissolve it in aqua regia. Boil off the chlorine, dilute, and pass H_2S. Determine the Hg as HgS in usual manner (see page 577).

As.—Acidify the alkaline solution containing As, Sb, Sn and pass H_2S. Filter the precipitate and wash with H_2S water. Transfer the precipitate to a beaker and add warm concentrated HCl. The Sb and Sn dissolve. Thoroughly wash the As sulfide. Dissolve it in aqua regia and determine the As as magnesium pyro-arsenate (see page 96).

Sb.—The solution from the arsenic is now combined with the filtrate *B* (above). Add NaOH and bromine (drop by drop) to oxidize all the sulfur (present as Na_2S). Acidify and boil the solution to remove excess of bromine. While still boiling add *ferrum-redactum* to precipitate the Sb (Sn is not reduced). Filter through a small filter besprinkled with the iron. Wash with dilute HCl. Reserve filtrate (*C*) for Sn. Transfer the Sb to a beaker and dissolve it in HCl (hot), adding a little bromine. Boil off the excess bromine. Add KI and H_2SO_4 to reduce the $SbCl_5$ to $SbCl_3$. Precipitate the Sb as Sb_2S_3 and determine it electrolytically (see page 73). If the amount of Sb is small, determine it gravimetrically as Sb_2O_4 (see page 72) or colorimetrically by the $KMnO_4$ method.

Sn.—Take the filtrate *C* from the "antimony-tin separation." Pass H_2S gas, filter off the tin-sulfide and determine as SnO_2 (see page 959).

Zn.—Take the filtrate *D* reserved from the precipitation of Hg, Sb, Sn, and As. Boil off the H_2S. Make alkaline with NH_4OH. Add formic acid. Pass H_2S, and allow the ZnS to settle out. Filter, and wash with H_2S water containing a little formic acid. Ignite and determine as ZnO, or by any other standard method described under Zinc. (See page 1058.) (Reserve filtrate for Fe, Al, Cr. etc.)

Fe, Al, Cr.—Boil off H_2S. Oxidize and precipitate Fe, Al, Cr. Separate by standard methods (see page 467).

Ca.—Take the ammoniacal filtrate from Group III (*a*). Evaporate, acidify with acetic acid, boil and precipitate the calcium as oxalate. Determine as CaO (see page 210).

Mg and Alkali Metals.—Take the filtrate from Ca, acidify with H_2SO_4. Ignite to decompose the NH_4 salts. Dissolve in 1% H_2SO_4. Filter into a platinum crucible. Ignite to drive off excess of H_2SO_4. The residue may contain $MgSO_4$, K_2SO_4, Na_2SO_4.

Weigh "Total residue." Dissolve in hot water and precipitate the Mg with ammonium phosphate. Determine Mg as pyrophosphate (see page 532). Recalculate the Mg to sulfate and subtract from the "Total residue." Calculate the difference to Na_2O.

Silica and Silicates.—(Powdered glass, pumice, kaolin, infusorial earth, etc.) Silica is most conveniently determined alone on the original material.

Take 1 g. and fuse in a Pt crucible with about 6 g. of a mixture of K_2CO_3 and Na_2CO_3 (equal parts). (Before using a platinum crucible for the fusion of rubber compounds it is always advisable to *test for Pb*. If lead is present use a porcelain crucible.)

Cool the melt. Leach with water. Boil and filter. Wash. Acidify with HCl. Evaporate the filtrate to dryness. Bake at 135° C. Add 5 ml. concentrated HCl. Evaporate dry, and again bake at 135° C. for one hour. Add 5 ml. concentrated HCl and dilute with H_2O. Filter and wash.

Ignite in a platinum crucible and weigh as SiO_2 (test its purity as on page 801).

VERMILION IN RUBBER GOODS

In absence of other metals of second group.[7]

Weigh out 0.5 g. sample, place in 500-ml. Kjeldahl flask, add 25 ml. concentrated H_2SO_4, and 3 g. K_2SO_4. Boil over a bunsen burner until solution is colorless. Bumping may be prevented by adding a few pieces of paraffin. Cool, and wash into a 400-ml. beaker. Add water until volume is about 250 ml. Heat on hot plate and pass H_2S through hot solution until precipitation is complete. Filter off the sulfide, wash precipitate back into the beaker, add 200 ml. of water and 2 g. Na_2SO_3 and boil for ½ hr. to dissolve out free sulfur. Filter the precipitate through a weighed Gooch, wash with hot water, dry at 100–105° C., and weigh as HgS.

HARD RUBBER (EBONITE)

This is analyzed in the same manner as soft-vulcanized rubber.

The sample is rasped to fine powder of which 2 g. are taken and extracted with acetone for 72 hours. The acetone extract is treated as for soft rubber, i.e., find weight of total extract and the sulfur in it is determined as usual. The difference gives the "organic" acetone extract. Rubber as used for ebonite contains about 4% resins; therefore if this figure is exceeded, it is probable that resins have been added and these may indicate that all the added resins have not entered the acetone extract.—Amber and shellac are insoluble in acetone, and are frequently used in hard rubber. It is recommended that the residue from the acetone extraction be extracted with epichlorhydrin (B.P. 170° C.) which will dissolve the amber, shellac, copal, and dammar resins if present. The extract obtained is evaporated and the weight determined. (Determine the sulfur.) Extract the residue with chloroform, and determine the extract as usual.

The residue from the chloroform contains the rubber-hydrocarbon combined with sulfur and the inorganic fillers (also sulfur in fillers). Determine the inorganic fillers by careful incineration.

[7] Methods of the American Hard Rubber Company, by courtesy of D. E. Jones, Chief Chemist.

Determine the sulfur in the residue from the chloroform, and subtract the sulfur in the mineral fillers. The difference gives the sulfur combined with the rubber itself (i.e. sulfur of vulcanization). The inorganic constituents are determined in the ash in a manner similar to that described for soft vulcanized rubber.

The amount of rubber is found by difference.

RECLAIMED RUBBER ("REGENERATED RUBBER")

A quantitative determination of the amount of "reclaim" in a vulcanized rubber compound is impossible, and all that can be done is to make deductions. For instance, "reclaim" yields a large acetone extract and therefore any abnormally high value for this extract points to either the use of reclaimed rubber, or oil surrogates, or added resin. The almost universal use of organic accelerators may so lower the vulcanization coefficient of the rubber mix that any abnormally high sulfur figure for the reclaim itself would be masked.

The examination of "reclaim" is carried out by the ordinary methods of analysis for vulcanized rubber.

Good quality "Reclaim" should not yield more than 10% to acetone. Asphalt is found by extraction with chloroform as for soft vulcanized rubber.

(For tests on "Reclaim" see Ind. Eng. Chem., **15**, 308–313 (1923) and Circular No. 232, Bureau of Standards, Washington.)

The following table gives the highest and lowest figures for usual qualities of commercial whole-tire reclaim:

Specific gravity	1.16 to 1.26
Moisture (max.)	1.0%
Alkalinity (4 hrs.)	0.15%
Acetone Extract	7–10%
Alc. KOH Extract	2%
Chloroform Extract	20–28%
Ash	18–25%
Tensile Strength	600–1000 lbs. per sq. inch
Elongation	300–500%

GUTTA PERCHA AND BALATA

Gutta percha is obtained from the latex of certain plants belonging to the Natural Order, *Sapotaceae*, growing wild in the Malay Peninsula, Sumatra and Borneo.

The true gutta percha (and the best quality) is obtained from the tree,

Palaquium oblongifolium, although allied species give a similar, but inferior, product.

Balata is obtained from the tree, *Mimusops globosa*, growing abundantly in Venezuela and the Guianas.

The hydrocarbon of gutta percha and balata is somewhat similar (but with very important differences) to that of rubber. A larger proportion of resin (acetone-extractable material) is associated with the two former, amounting frequently to 50%. Gutta percha as extracted from leaves, at Tjipetir, by the petrol-solution method and subsequent chilling, is almost white in color, and contains only about 1% of resin. When cold, the gutta and balata hydrocarbons are hard and tough like leather. They are thermoplastic, while resilience (as exhibited by rubber) is almost entirely absent.

Gutta percha is used chiefly for submarine-cable insulation material, moldings, surgical and chemical utensils (HF containers) whilst balata is a useful ingredient of belting. Although gutta and balata can be vulcanized their value is not increased thereby.

These two materials are therefore used after being carefully washed, strained and dried. Compounding ingredients are sometimes added, and the material is often deresinated in order to produce harder products.

(For a full account of Guttapercha, see Obach, Cantor Lectures, J. S. A., **8** (1897).)

As the supply of good guttapercha is becoming restricted, the price is rising ($2.00 per lb. for best quality) and therefore adulteration or substitution is not infrequent.

The price of Balata on the other hand remains about 50 cents per lb. and there seems at present an ample supply.

Sampling.—It is almost impossible to obtain from a case of gutta percha a truly representative sample fit for chemical analysis. The material arrives in lumps of all manner of shape and is not homogeneous.

Washing Loss.—The only satisfactory way to arrive at the washing loss is to wait until the whole consignment has passed through the factory washing and drying processes. Calculate " washing loss."

Analysis of Gutta Percha and Balata.—The usual determinations required are: Moisture, resin, dirt, gutta-hydrocarbon.

Moisture.—Cut up the sample (a thin sheet from bulk) into snippets and mix. Take 3–5 g. in a flat dish, and dry in vacuo at 75° C. for six hours; or the material may be warmed in a current of dry CO_2.

Resin.—(Acetone-extract.)

(Note: Acetone is the best solvent for the extraction of resins from gutta percha and balata. Ether dissolves a part of the gutta or balata, thus giving high results for " resins," whilst with alcohol the gutta hydrocarbon becomes thermoplastic on account of the relatively high boiling point of the solvent, the snippets coalesce and the extraction is therefore incomplete.) Take a 2 g. sample of the snippets and extract with acetone for 6 to 12 hours by the method described for raw rubber (page 1969). Evaporate the solvent, and dry the extract at 110° C. to constant weight. Both the extract and the residue from acetone are liable to oxidation. Therefore the drying is preferably performed in a vacuum desiccator, heated electrically; or in an inert gas.

The resins of gutta percha and balata are a mixture of white and yellow resins. The white resins (Albanes) are soluble in **hot** alcohol (not in cold). They are crystalline and have a composition approximating to $C_{17}H_{26}O$. The yellow resins (Fluavils) are amorphous and are soluble in **cold** alcohol as well as hot.

This difference in solubility affords a method of separation if required.

Gutta (and Balata) Hydrocarbon.—(Rapid Method.) Boil 1 g. of the sample with 20 ml. redistilled toluene. Heat to 100° C. on a water-bath until dissolved.

Pour the solution into 50 ml. alcohol (95%). Allow the contents of the vessel to stand for a few hours. Warm and agitate to clear the liquid. Remove, redissolve in toluene and reprecipitate by alcohol. Dry the hydrocarbon in vacuo and weigh in a closed weighing bottle. The hydrocarbon may also be calculated by difference as for rubber-hydrocarbon.

Dirt.—This is generally under 0.5% for washed and strained material after the factory cleaning process. The dirt consists of both organic and inorganic debris. The inorganic matter may be determined by incinerating a 1 g. sample of the original material.

The " organic " debris consists of fine particles of bark. If this determination is required a solvent method must be employed and when the residue is obtained it should be weighed (organic and inorganic dirt) and ignited to obtain mineral (weigh). Subtract the latter from the former weight and thus determine the organic debris. The " dirt " should be examined for ZnO, lithopone, antimony sulfide and carbon.

Obach gives the following range as typical of Gutta Percha.

Water	1–1.5%
Dirt	3–5%
Gutta Hydrocarbon	30–83%
Alban	7–44%
Fluavil	3–21%
Ash, max.	0.5%

The average composition of balata (ordinary quality) is as follows:

Water	7%
Dirt	10%
Resins	39%
Balata Hydrocarbon	43%

After washing:

Balata Hydrocarbon	52%
Resins	47%
Water	1%

Separation of Balata and Rubber, or Gutta Percha and Rubber.—The gutta (and balata) hydrocarbon is insoluble in petroleum ether below 0° C., whereas the rubber hydrocarbon and resins remain soluble. This fact (which forms the basis of the process for producing leaf gutta at Tjipetir, Malay) is used as the means of separation required.

The rubber containing balata and (or) gutta percha is dissolved in warm petroleum-ether. The solution is then chilled to about *minus* 16° C. The balata (gutta percha) hydrocarbon is precipitated as a white flocculent solid.

Charleson's Method for separating gutta percha (balata) hydrocarbon from rubber (as in compounds for golf ball covers). Mix the sample on the mixing rolls and then make a very thin sheet. Of this take about 3 g. and dissolve it in a flask containing 200 ml. of petroleum ether. Warm on a steam bath with frequent agitation. When the whole is in " solution " allow the flask to cool to room temperature and then place it in a freezing mixture capable of producing a temperature of −12° C.

The balata (or gutta) hydrocarbon is precipitated, while the rubber and resins remain in solution.

Filter the contents of the flask through a funnel surrounded by a freezing mixture and wash with ice-cold petroleum ether. Collect the precipitate and dry it in an electrically heated vacuum desiccator. Weigh the dried residue.

PHYSICAL TESTS

As previously mentioned chemical analysis of rubber (raw and manufactured) should be supplemented by physical tests. Analytical determinations are of value for the evaluation of raw rubber, yet may be inadequate for judging quality and technical value unless accompanied by mechanical and vulcanization tests (i.e., rate of cure and quality of the vulcanizate).

The **mechanical tests** carried out include the determination of the stress-strain relations (modulus) on stretching and compression hysteresis (repetition of stretch and release). (The technique of the tensile tests, etc., are fully discussed by G. S. Whitby in " Plantation Rubber and the Testing of Rubber " and deals in detail with the interpretation of results.)

The technique of **vulcanization tests** involves a " type-mixture " and the standardization of the conditions of vulcanization so that any new consignment of rubber may be compared under identical conditions in different laboratories or be compared with a known quality.

Considerable care must be exercised in the **preparation of the sample for test.** A standard temperature (70° C.) should be maintained upon the masticating rolls. The ' nip ' should be fixed at a standard distance according to the size of the batch, and a constant temperature is set for vulcanization (press or autoclave),

The test-pieces may be either dumb-bell shaped or rings.

For **mechanical testing,** rings are often preferred although there is difference of opinion respecting their relative value. The rings are generally used in a ' Schopper Machine ' which possesses two rotating cylinders whose distance apart may be increased gradually while the pull (load) and elongation are pro-

gressively recorded autographically, thus producing a stress-strain curve. The advantage of ' rings ' over the dumb-bell shaped test-pieces lies in the fact that the difficulties incurred with grips (which slip, or tear the sample) are obviated. Also, as the tensile strength and elongation at the moment of break are less important than the stress-strain curve throughout the stretch an autographic recording device is essential and this is provided on the ring-testing machines. Nevertheless, errors due to rings exist due to the fact that although the stress measured by the ring-test is the average, the elongation is that of the inner edge only. But a more serious error may arise with test-rings cut from calendered sheet which possess a distinct grain and shows its greatest tensile strength in the direction parallel to this grain. Rings will break at their weakest point (across the grain) whereas " dumb-bell " test-pieces may be cut so as to enable mechanical tests to be carried out in any direction.

Ageing Tests may be conducted in a Geer oven, or by the method of Bierer and Davis, which provide accelerated ageing under scientific conditions.

Abrasion Tests (on tire-tread material, etc.) may be carried out by running a ball (cut from the material) in a V-shaped groove under a given load at a fixed speed. The ball is tested to destruction.

Permanent Set indicates the quality of the " cure." Properly vulcanized rubber should show no permanent set after a reasonable period of rest (10 minutes). The test is made by measuring the distance between fine gauge marks upon the narrow portion of the dumb-bell test-piece, before and after stretching.

The stress-strain curve of rubber is unique and is exactly opposite in character to that of metals which follow Hooke's Law. Schidrowitz has demonstrated that the hysteresis loops are characteristic; strong firm rubbers show long flat loops which become constant after the second cycle, whereas soft rubbers give upright loops of small area.

Attempts to determine quality numerically are not exact, but lead to useful comparisons. Two " characteristics " are frequently used, viz., the **" Tensile Product "** and **" Slope."**

The Tensile Product of a vulcanizate is a number obtained by multiplying the tensile strength at break by the ratio of final length at break to the original length of the test-portion. (Thus, in metric units, if the ultimate strength is 1.3 kg. per sq. mm., and the final length between the gauge-marks is 700% of the original, then the Tensile Product is 9.1.)

The Slope is the **rate** at which increasing load increases the extension and represents the resistance to stretching at high elongations.

The **Friction-Pull Test** measures the adhesion existing between the layers of rubber-coated fabric. Two standard methods are employed.

(1) The dead-weight method: strips 1 in. wide are mounted in a clamp. The ply is separated a sufficient distance to enable weights to be loaded until the layers begin to separate. The load required to cause a separation of 1 in. per minute is taken as the " friction-pull."

(2) Test-machine method: The ends of the separated plies are gripped in opposing jaws which are drawn apart at the rate of 2 in. per minute. The friction-pull is recorded on a dial, or autographically.

The conditions laid down for physical-testing and recommended by the Rubber Div. of the Amer. Chem. Soc. to be adopted as standard by all Testing Laboratories are as follows (see Rubber Chem. and Tech., 3, 179 (Apr. 1930)).

Mill Data: Rolls 12 in. × 6 in.; working distance between the cheeks 10½ in.; speed of slow roll = 24 r.p.m.; gear ratio 1 : 4; temperature of rolls during mastication = 70° C. The " nip " will vary with the volume of the batch (i.e. for 800 ml. use a nip ⅛ in. wide, etc.).

Mixing: All ingredients to be weighed to 0.25%. During mastication the " nip " shall be .055 in. until the rubber runs smooth—then open out as volume increases.

Order of Adding Ingredients: Accelerators, antioxidants, blacks, fillers, softeners, sulfur.

Storage of Batch: Stack for 24 hours on a galvanized-wire netting, in the dark at 27° C. and a relative humidity of 45%. (Variation in humidity causes great variation in tensile strength.)

Preparation of the Stock for Curing: Cut with a die ⅛ in. less in length and width than the mold cavity—the grain of the material should run parallel to the length of the mold.

Curing Temperature: The temperature inside the mold should be registered by means of a thermocouple. The platens should be bored and good drainage should be secured to avoid cold spots.

Time of Cure: This should start from the time the hydraulic pressure reaches the prescribed maximum, and end at its release. The mold should be pre-heated for 20 minute and should be shielded by felt during the cure.

Molds: No " preparation " of any sort need be used to prevent sticking. The molds may be cleaned when necessary with ground emery and water.

Cooling of Cured Test-pieces: Place the specimens immediately in cold running water to cool for ten minutes. When cool, wipe dry and store on wire-net in the dark.

Die-ing of Specimens: Wet with water and cut to standard size (dumb-bell shaped specimens are recommended).

Temperature of Mechanical Test: 27° C. ± 2° C.

Speed of Test: A Scott Testing Machine is recommended, travelling at 20 inches per minute.

Results: Breaks outside the narrow straight portion of the specimen are discarded. Take the highest figure together with those within 5% and take the average.

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RUBBER COMPOUNDS AND COMPOUNDING INGREDIENTS [1]

The analytical side of rubber chemistry falls naturally into two divisions:

1. Analysis of rubber compounds, either vulcanized or unvulcanized.
2. Analysis of raw materials, including rubber, softeners, fillers, etc.

Most of the analyses in the first class require special technique, and while many of those in the second class are common in other lines, the proper interpretation of analytical results involves some knowledge of rubber chemistry and compounding practice.

Samples of rubber compounds are usually analyzed for one of four purposes:

1. To check conformity to chemical specifications.
2. To determine the composition for purposes of duplication.
3. To determine the state of "cure" of a compound of known properties.
4. To check the proper weighing or mixing of a batch.

Many methods have been published for the various determinations required, but after extensive conferences and testing, the following methods for the common determinations have been recommended by the Division of Rubber Chemistry of the American Chemical Society and the A. S. T. M.[2] Other methods and special determinations will be found in a subsequent chapter.

STANDARD METHODS FOR THE ANALYSIS OF RUBBER GOODS [3]

Reasons for the Analysis

Acetone Extract.—If the acetone extraction is made on a vulcanized compound, the acetone removes the rubber resins, the free sulfur, any mineral oils or waxes, and part of any bituminous substances or vulcanized oils that may have been used. The percentage of free sulfur is determined and deducted from the total extract. The corrected figure thus obtained will at times give

[1] By Raymond B. Stringfield Consulting Chemical Engineer, Sec'y Dental Plastic Co., Los Angeles. Formerly Chief Chemist, Goodyear Tire and Rubber Company of Calif.

[2] Ind. and Eng. Chem. **16**, 397 (1924). Book of A. S. T. M. Standards, 1933. Part II.

[3] Approved by the Supervisory Committee on Standard Methods of Analysis, American Chemical Society, March 1, 1924.

valuable information regarding the quality of the rubber present. For the best grades of Hevea rubber, this corrected extract should not exceed 5% of the rubber present. A higher extract may indicate the presence of inferior or reclaimed rubbers.

Chloroform Extract.—The chloroform extraction removes a portion of the bituminous substances and serves as an indication of their presence.

Alcoholic-Alkali Extract.—The purpose of the alcoholic-alkali extraction is to detect the presence of rubber substitutes.

Free Sulfur.—The free sulfur is defined as that which is removed during the acetone extraction.

Total Sulfur.—This represents the sulfur that occurs in the compound either free or chemically combined.

Ash.—The ash is the residue left after ignition, and consists principally of the nonvolatile mineral fillers, together with their reaction products with sulfur.

Sulfur in Ash.—The sulfur in ash consists of the sulfur from the mineral fillers, and also part of the sulfur that was with the rubber, but which during ignition enters into combination with one or another of the mineral fillers.

Special Determinations.—Special methods are given for the analysis of compounds that contain glue, carbon, antimony, and waxy hydrocarbons.

Rubber.—Up to the present time no simple method has been devised for the direct determination of the amount of rubber present in a vulcanized compound. Therefore, an indirect method is proposed which will give satisfactory results in all cases known to-day, except where there are found to be present decomposable fillers, such as carbonates, cellulose, and high percentages of mineral rubbers. As practically all insulating compounds contain some of these ingredients, the said compounds when specified shall be analyzed in accordance with Joint Rubber Insulation Committee's method, as given in Paragraph 34.

When carbonates, talc, and asbestine are present, more accurate results are obtained by the use of the Joint Rubber Insulation Committee's methods given in Paragraph 34.

If high percentages of mineral rubber are used, no accurate method is known. If cellulose is present, the best results are obtained by the method given in Paragraph 35.

Preparation of Sample

1. Before preparing a sample for analysis, the analyst shall, by inspection, assure himself that it has not been contaminated. The sample shall be prepared by taking pieces from various parts of the original sample and separating them from foreign matter.

2. The pieces shall be ground to the required fineness on a rubber mill or cut with scissors so as to pass a No. 14 sieve.

3. Hard rubber should be prepared by rasping with a coarse file, cleaning with a magnet, and passing through a No. 14 sieve.

4. Crude, reclaimed, or unvulcanized rubber shall be sheeted out very thin on an experimental mill, and shall be rolled in holland or other cotton cloth to prevent the sample from sticking. If no mill is available, the sample shall be cut as fine as possible with scissors.

5. Samples of rubberized cloth shall be prepared by cutting into pieces 1.5 cm. square and then mixing well.

6. Cements: Cements shall be evaporated to dryness and the residue analyzed as an unvulcanized sample. A separate sample shall be steam-distilled if examination of the solvent is desired.

Reagents

7. The acetone shall be chemically pure and shall be freshly redistilled over anhydrous sodium carbonate, using the 56° to 57° C. fraction.

8. The alcoholic-alkali solution shall be of normal strength. It shall be made by dissolving the required amount of alkali (either potassium or sodium hydroxide) in the smallest quantity of hot, distilled water and adding this to specially purified alcohol, which shall be prepared as follows:

Dissolve 1.5 g. of silver nitrate in 3 ml. of water, and add it to 1000 ml. of alcohol. Dissolve 3 g. of alkali in the smallest amount of hot water, cool, add it to the alcoholic-silver nitrate solution, and shake thoroughly. Allow the solution to stand for at least 24 hrs., filter, and distil. (Alcohol denatured with 10% by volume of methanol may be used in place of ethyl alcohol.)

9. The nitric acid-bromine reagent shall be prepared by adding a considerable excess of bromine to concentrated nitric acid and shaking thoroughly. It can be used immediately.

10. The zinc oxide-nitric acid solution is made by adding 200 g. of zinc oxide to 1000 ml. of concentrated nitric acid.

11. Barium chloride solution shall be made by dissolving 100 g. of crystallized barium chloride in 1 liter of distilled water and adding 2 to 3 drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness, the solution shall be heated over night on the steam bath and filtered. Care should be taken not to add more acid than the amount specified.

12. Standard 0.1 N potassium permanganate solution shall be made as follows:

Dissolve approximately 3.1 g. of potassium permanganate in 1 liter of water, and when it is dissolved filter through an ignited asbestos pad. Weigh out 0.25 g. of pure metallic antimony and transfer to a 600-ml. Erlenmeyer flask. Add 12 to 15 ml. of concentrated sulfuric acid, 10 to 12 g. of potassium sulfate, and heat until all the antimony is dissolved. Dilute to 250 ml. with water, add 20 ml. of concentrated hydrochloric acid, cool to 10° to 15° C., and titrate with permanganate solution until a faint pink color is obtained.

$$1 \text{ ml. of } 0.1 \text{ N } KMnO_4 = \frac{\text{Wt. of metallic antimony}}{\text{Ml. of permanganate}} = \text{wt. of antimony.}$$

13. Starch-iodate paper shall be prepared by impregnating filter paper with a solution obtained by heating 2 g. of starch with 100 ml. of water and, after solution, adding 0.2 g. of potassium iodate dissolved in 5 ml. of water.

14. A Gooch crucible shall be prepared in the following manner:

Cut amphibole asbestos fine with shears, digest with 10% caustic soda solution, wash with water, and then digest with concentrated hydrochloric acid for a few hours on the steam bath. After it has been washed comparatively free from acid by decantation, shake up the asbestos with water and use

the resulting mixture in preparing the pads. The Gooch crucibles should be ignited, and are then ready for use.

15. The purity of all material shall be checked and determined by blank analyses.

Methods of Analysis

16. **Specific Gravity.**—This shall be determined by the use of a pycnometer, using alcohol in place of water to eliminate the errors due to air bubbles.

A = Wt. of pycnometer filled with alcohol,
B = Wt. of pycnometer filled with sample and alcohol,
C = Wt. of sample.

$$\text{Sp.gr.} = \frac{C}{C-(B-A)} \times \text{Sp.gr. of alcohol.}$$

17. **Acetone Extract.**—The extracting apparatus used here and for other extractions shall be of the type similar to that shown on page 1970. (See also Industrial and Engineering Chemistry, 9, 314 (1917).) The flask shall be heated so that the period of filling an empty siphon cup with acetone and completely emptying it will be between 2.5 and 3.5 min.

Place 2 g. of rubber in a thimble made by folding a filter paper so that it will fit in the extraction cup, which is suspended in a weighed extraction flask. Extract the sample continuously for 8 hrs., unless the solution in the thimble is still colored at the end of that time, when the extraction shall proceed for a further period of 4 hrs. or longer. For hard rubber the extraction period shall be a minimum of 72 hrs. Carefully note all characteristics of the acetone extract, both when hot and cold. Distil off the acetone on the steam bath at as low a temperature as possible. Loss of extract by bumping can be avoided by means of a gentle current of air or by slightly inclining the flask.

Care must be taken to avoid allowing the flasks to stand on the steam bath after the solvent has been removed, because appreciable quantities of free sulfur may be lost by so doing. Dry the extraction flask and contents in an air bath for 1 hr. at 70° C., cool, and weigh. Call the residue "Acetone Extract, Uncorrected."

$$\text{Percentage of acetone extract, uncorrected} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

Save the rubber sample and keep for future determination.

18. **Chloroform Extract.**—The rubber sample (Paragraph 17), without removing the acetone from it, is suspended in a second weighed extraction flask and extracted for 4 hrs. with chloroform. Care should be taken that any small particles of rubber, which are often carried down into the extract, are filtered off. Evaporate off the solvent and dry the residue to constant weight—usually 1 hr. at 70° C.—cool, and weigh. The color of the chloroform solution should be recorded. Reserve the rubber for extraction with alcoholic-alkali.

$$\text{Percentage of chloroform extract} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

19. **Alcoholic-Alkali Extract.**—Dry the rubber from the chloroform extraction at about 70° C. to remove the chloroform, transfer to a 200-ml. Erlenmeyer flask, add 50 ml. of alcoholic-alkali solution, and heat under a reflux condenser for 4 hrs. Filter into a 250-ml. beaker, wash with two portions of 25 ml. each of boiling alcohol, then with three 25-ml. portions of boiling water, and evaporate the filtrate to dryness. Use about 75 ml. of distilled water to transfer the residue to a separatory funnel. Acidify the solution with 10% hydrochloric acid, testing with Congo red paper. Extract with four 25-ml. portions of ether, unless the fourth portion is colored, when the extraction must be continued until no further quantity can be removed. Unite the ether fractions and wash thoroughly with distilled water until free from acid (two washings are generally sufficient). Filter the ether solution through a plug of absorbent cotton into a weighed flask, wash with ether, evaporate, dry to constant weight at 70° C., cool, and weigh.

$$\text{Percentage of alcoholic-alkali extract} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

20. **Free Sulfur.**—Add to the flask containing the acetone extract, uncorrected (Paragraph 17), 50 to 60 ml. of distilled water and 2 to 3 ml. of bromine, and cover with a watch glass. (If the acetone extract indicated a large amount of free sulfur, the amount of bromine used may be increased.) Allow the flask to stand 0.5 hr. on the side of the steam bath, then heat cautiously over the direct steam bath until the solution is practically colorless, filter into a 250–ml. beaker, and dilute to about 175 ml. with distilled water. Precipitate with barium chloride and determine in the usual manner, taking the proper precautions to prevent the reduction of the barium sulfate during the ignition.

$$\text{Percentage of free sulfur} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

21. **Total Sulfur.**—Place 0.5 g. of rubber in a porcelain crucible of about 75 ml. capacity, add 15 ml. of the nitric acid-bromine mixture, cover the crucible with a watch glass, and let it stand for 1 hr. in the cold. Heat for an hour on the steam bath, remove the cover, rinse it with a little distilled water, and evaporate to dryness. Add 3 ml. of nitric acid, cover, warm a short time on the steam bath, then let it cool. Carefully add in small portions, by means of a glass spatula, 5 g. of sodium carbonate (weighed to 0.5 g.). The watch glass is to be raised only high enough to permit the introduction of the spatula. The carbonate is allowed to slide down the side of the crucible and is not dropped directly into the acid. Rinse the watch glass with 2 or 3 ml. of hot distilled water and stir the mixture thoroughly with a glass rod. Digest for a few minutes, spread the mixture halfway up the side of the crucible to facilitate drying, and dry on a steam bath. Fuse the mixture by heating over a sulfur-free gasoline flame.

Place the crucible in an inclined position on a wire triangle and start the ignition over a low flame. The tendency for the rubber to burn too briskly is controlled by judicious use of the stirring rod with which the burning portion is scraped away from the rest. When part of the mass is burned white, a fresh portion is worked into it, and so on until all of the organic matter is

destroyed. It is necessary to hold the edge of the crucible with tongs. Toward the last half of the operation the flame should be increased somewhat, but it is never necessary to heat the crucible to redness. With care a crucible can be used for at least ten or twelve fusions.

After a fusion, allow the crucible to cool, place it in a 400-ml. beaker, add sufficient distilled water to cover the crucible (about 125 ml. are required), and digest on the steam bath for 2 hrs., with occasional stirring. If the filtration cannot be made in the same day, do not add the water, but allow the fusion to stand over night.

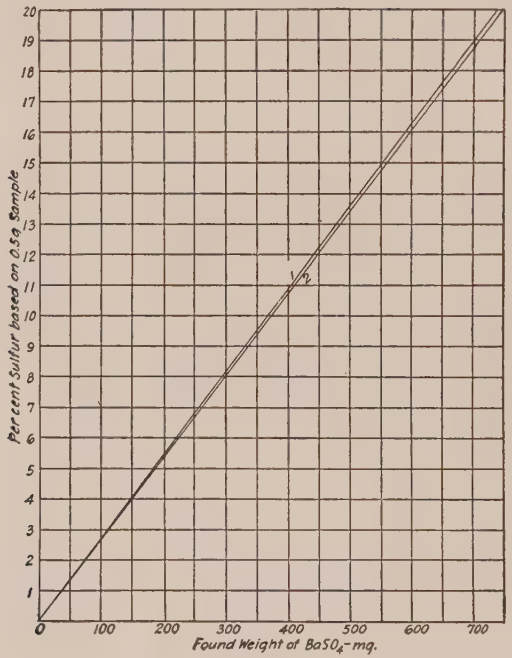


FIG. 286.

Filter the solution into a covered 400-ml. beaker containing 5 ml. of concentrated hydrochloric acid, and wash the residue thoroughly with hot water. (A qualitative test for barium sulfate can be made on the residue.) Now complete the acidification of the filtrate and washings in the cold and add 2 ml. of concentrated hydrochloric acid in excess. Cover the beaker and heat the solution on the steam bath. The total volume of the solution should not exceed 300 ml. The solution must be acid to Congo paper in order to insure the complete destruction of the carbonates. Precipitate with barium chloride and determine the sulfur in the usual manner.

$$\text{Percentage of total sulfur}^{4} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

[4] To correct the sulfur for occlusion use Graph 1, line marked 2.

22. **Alternative Method.**—When this method is used, the total sulfur determined represents the sulfur exclusive of that as barytes, if used in the compound.

Place a 0.5-g. sample in a 500-ml. Erlenmeyer destruction flask (Pyrex glass). Add 10 ml. of zinc oxide-nitric acid solution and whirl the flask rapidly to moisten the sample thoroughly. If convenient, the mixture may be allowed to stand over night at this point. By so doing the sample becomes partly decomposed; this permits the addition of fuming nitric acid with no danger of ignition of the sample. Add 15 ml. of fuming nitric acid and whirl the flask rapidly to keep the sample immersed to avoid ignition by too rapid oxidation. With some samples it will be found necessary to cool the flask under a stream of tap water.

When the solution of the rubber is complete, add 5 ml. of saturated water solution of bromine, and slowly evaporate the mixture to a foamy sirup. (For the determination of total sulfur in unvulcanized mixtures use 3 ml. of bromine in place of bromine water.)

If particles of organic matter remain at the end of the evaporation, add a few ml. of fuming nitric acid, and reëvaporate as before. Cool, and add a few crystals of potassium chlorate to assist in the oxidation of the sulfur and the decomposition of any nitrates.

Place the flask on asbestos gauze and evaporate the mixture to dryness over a Tirrill burner. Then bake the mixture at the highest temperature of the burner until all nitrates are decomposed and no more nitrogen peroxide fumes can be detected. (Care should be taken to insure uniform penetration of the heat throughout the contents of the flask and to remove the flask as soon as the "baking" is complete.) When the baking is complete, cool the flask, add 50 ml. of (1 : 6) hydrochloric acid, and heat until solution is complete. (In case the original mixture contains barium salts, they will be precipitated at this point. If litharge is present in the mixture, lead salts, not otherwise removed, will be eliminated in the final washing with boiling water.) Filter the solution, dilute to 300 ml., precipitate with barium chloride, and determine the sulfur in the usual manner.

$$\text{Percentage of total sulfur}^{5} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

23. **Ash.**—Wrap a 1-g. sample in a filter paper, extract with acetone for 4 hrs., and transfer to a weighed, approximately 50-ml. porcelain crucible. Ash the sample in a muffle furnace by heating at the following rate:

Time, min.	0	5	10	15	70	75	80	85	145
Temp., ° C.	0	100	200	300	300	400	500	550	550

Remove crucible from the furnace, cool, and weigh.

If no furnace is available, distil off the rubber over a very small flame, not allowing it to catch fire, and ignite gently until burned clean, cool, and weigh.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash}}{\text{Wt. of sample}} \times 100.$$

[5] To correct the sulfur for occlusion use Graph 1, line marked 1 (figure 286).

24. **Sulfur in Ash.**—Add 3 ml. of nitric acid-bromine mixture to the ash (Paragraph 23), cover with a watch glass and heat for 1 hr., remove the cover, rinse it with a little distilled water, and evaporate to dryness. Complete the determination of sulfur as described under Paragraph 21.

$$\text{Percentage of sulfur in ash } [5] = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

Save the insoluble residue after filtering the solution of the fusion mixture in water for testing according to Paragraph 25.

25. **Barium Sulfate.**—The barium sulfate is calculated from the barium in the ash, which is determined as follows: Filter off the insoluble matter after the fusion and extraction in Paragraph 24, wash back into the original beaker with hot water, dissolve the residue in the beaker and any traces on the filter paper with hydrochloric acid, and heat the solution on the steam bath. Filter through the same filter as before and wash thoroughly with hot water. Nearly neutralize the solution with ammonium hydroxide, leaving it slightly acid. Saturate the solution with hydrogen sulfide in the cold, and when the lead sulfide has settled, filter into a 400-ml. beaker and wash thoroughly. The total volume should be not over 200 ml. Precipitate with 10% sulfuric acid and determine the barium in the usual manner. Barium sulfate determined above is assumed to have been added as such. Obviously, if barium carbonate is used, it must be determined in order that an undue correction shall not be made.

$$\text{Percentage of sulfur as barium sulfate} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

26. **Total Antimony.**—When a qualitative test indicates that antimony is present, place a 0.5-g. sample, and transfer in a Kjeldahl flask, add 25 ml. of concentrated sulfuric acid and 10 to 12 g. of potassium sulfate, place a funnel in the neck of the flask, and heat until the solution becomes colorless. Cool and wash the funnel, dilute the solution to 100 ml. with water, and transfer to a 400-ml. beaker, dilute to 250 ml. with hot water, and precipitate the antimony with hydrogen sulfide. Filter and transfer the precipitate to a Kjeldahl flask, add 15 ml. of concentrated sulfuric acid, 10 to 12 g. of potassium sulfate, and heat as described above until the solution is colorless. Wash the funnel, dilute the solution to 100 ml. with water, add 1 to 2 g. of sodium sulfite, and boil until all the sulfur dioxide is driven out. This is shown when no blue color is obtained with starch iodate paper. Add 20 ml. of concentrated hydrochloric acid, dilute to 250 to 275 ml. with water, cool to 10° to 15° C., and titrate with standard 0.1 N permanganate solution until a faint pink color is obtained. If iron is found to be absent, it is not necessary to precipitate the antimony with hydrogen sulfide, and the second heating in a Kjeldahl flask can be eliminated.

$$\text{Percentage of antimony} = \frac{\text{Sb (Paragraph 12)} \times \text{ml. of permanganate}}{\text{Wt. of sample}} \times 100.$$

27. **Antimony in the Ash.**—This is determined in the ash of a 1-g. sample. Transfer the ash to a 600-ml. Erlenmeyer flask, add 12 to 15 ml. of concentrated

sulfuric acid and 10 to 12 g. of potassium sulfate, and boil until solution is complete. It may be necessary to warm part of the sulfuric acid in the crucible to transfer any adhering particles to the flask. Rinse with the remaining portion of acid. Then complete the determination as described in Paragraph 26.
Percentage of antimony as Sb_2O_4 in ash

$$= \frac{\text{Sb (Paragraph 12)} \times \text{ml. of permanganate} \times 1.26}{\text{Wt. of sample}} \times 100.$$

28. **Free Carbon.**—Extract a 0.5-g. sample for 8 hrs. with a mixture of chloroform and acetone in a volume ratio of 2 : 1. Transfer the sample to a 250-ml. beaker and heat on the steam bath until it no longer smells of chloroform. Add a few ml. of concentrated nitric acid and allow to stand in the cold for about 10 min. Add 50 ml. more of hot concentrated nitric acid, taking care to wash down the sides of the beaker, and heat on the steam bath for at least 1 hr. At the end of this time there should be no more bubbles or foam on the surface. Pour the liquid while hot into the crucible, taking care to keep as much as possible of the insoluble material in the beaker. Filter slowly with gentle suction and wash well by decantation with hot concentrated nitric acid. (Caution: Empty the filter flask.) Wash with acetone and a mixture of equal parts of acetone and chloroform until the filtrate is colorless. Digest the insoluble material, which has been carefully retained in the beaker, for 30 min. on the steam bath with 35 ml. of 25% sodium hydroxide solution. This treatment with alkali can be omitted if silicates are absent. Dilute to 60 ml. with hot distilled water and heat on the steam bath. Filter the solution of alkali and wash well with hot 15% sodium hydroxide solution.

Next wash the residue four times with hot concentrated hydrochloric acid. Neutralize the last washing with ammonia and test for the presence of lead with sodium chromate solution. If none is present, finally wash with warm 5% hydrochloric acid. Remove the crucible from the funnel, taking care that the outside is perfectly clean, dry it in an air bath for 1.5 hrs. at 110° C., cool, weigh, burn off the carbon at a dull red heat, and reweigh. The difference in weight represents approximately 105% of the carbon originally present in the form of lamp-black or gas black.
Percentage of free carbon

$$= \frac{\text{Wt. of crucible with carbon} - \text{wt. of crucible after ignition}}{1.05 \times \text{wt. of sample}} \times 100.$$

29. **Detection of Glue.**—Extract a 2-g. sample for about 6 hrs. with acetone. Then heat for 2 hrs. on the steam bath, with sufficient water to cover it, cool, filter, and pour slowly into a 1% solution of tannic acid. If a permanent cloudiness, however slight, appears, glue is present.

30. **Nitrogen Calculated as Glue.**—When glue is found to be present, a correction must be made for the natural protein in the rubber. The average amount of nitrogen is 0.4%. (See Paragraph 40 for calculations.)

Extract a 2-g. sample for 8 hrs. with acetone. Remove the solvent from the sample, and transfer the latter from the filter paper to a 750-ml. Kjeldahl flask. Add 25 to 30 ml. of concentrated sulfuric acid and 10 to 12 g. of sodium sulfate. Place the flask on the Kjeldahl digesting apparatus. Heat gently

until the first vigorous frothing ceases, then raise the heat gradually until the liquid boils. Continue the boiling until the solution becomes clear. Allow the flask to cool, dilute carefully with 150 ml. of water, and allow to cool. Add 100 ml. of 50% sodium hydroxide solution, pouring it carefully down the side of the flask so that it does not mix immediately with the acid solution. Add about 1 g. of granulated zinc to prevent bumping and a piece of paraffin the size of a pea to diminish frothing. Connect the flask quickly with a condenser, the delivery tube of which dips into a 500-ml. Erlenmeyer flask, containing 50 ml. of 0.1 N sulfuric acid diluted to about 100 ml. Carefully swirl the flask to mix the contents and start to heat gently, increase the flame as the danger of foaming over diminishes, and, finally, boil briskly until about one-half of the liquid has passed over into the receiver. Add methyl red solution and titrate the excess acid by means of 0.1 N sodium hydroxide solution. A blank determination should be made.

Percentage of nitrogen as glue

$$= \frac{100\ (\text{ml. } H_2SO_4 \times \text{normality} - \text{ml. NaOH} \times \text{normality})\ (0.014)\ (6.5)}{\text{Wt. of sample}}$$

$$= (\text{ml. } H_2SO_4 \times \text{normality} - \text{ml. NaOH} \times \text{normality}) \times 4.55.^{6}$$

31. **Unsaponifiable Matter.**—If this determination is made, the free sulfur shall be determined on a separate 2-g. sample.

Add to the acetone extract obtained from two 2-g. samples (Paragraph 17) 50 ml. of N alcoholic-alkali solution, heat on the steam bath under a reflux condenser for 2 hrs., remove the condenser, and evaporate to dryness. Transfer to a separatory funnel, using about 100 ml. of water, add 25 ml. of ether, and shake. Allow the two layers to separate thoroughly, then draw off the water layer. Continue the extraction of the water layer with fresh portions of ether until no more unsaponifiable matter is removed, unite the ethereal layers, and wash with distilled water. Transfer the ether to a tared flask, distil off the ether, dry to constant weight at 70° C., cool, and weigh.

$$\text{Percentage of unsaponifiable matter} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

32. **Hydrocarbons A.**—To the unsaponifiable matter (Paragraph 31) add 50 ml. of absolute alcohol, and heat on the steam bath for 0.5 hr. Let the flask stand in a mixture of ice and salt for 1 hr. Filter off the separated waxy hydrocarbons on filter paper by applying a gentle suction. Wash with alcohol (95% will do), which has been cooled in an ice-salt mixture. The funnel should be surrounded by a freezing mixture.

Dissolve the precipitate from the filter paper with hot chloroform, and catch the solution in a weighed 100- to 150-ml. beaker. Wash the flask with hot chloroform, which is added to the same beaker, in order to include any undissolved waxy matter adhering to the walls of the flask. Evaporate off the solvent, dry to constant weight at 70° C., cool, and weigh.

$$\text{Percentage of hydrocarbons A} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

[6] Simplified formula when a 2-g. sample is used.

33. **Hydrocarbons B.**—Evaporate the alcohol from the flask containing the alcohol-soluble unsaponifiable material, add 25 ml. of carbon tetrachloride, and transfer to a separatory funnel. Shake with concentrated sulfuric acid, drain off the discolored acid, and repeat with fresh portions of acid until there is no longer any discoloration. After drawing off all the acid, wash the carbon tetrachloride solution with repeated portions of water until all traces of acid are removed. Transfer the carbon tetrachloride solution to a weighed flask, evaporate off the solvent, and dry to constant weight at 70° C., cool, and weigh.

$$\text{Percentage of hydrocarbons B} = \frac{\text{Wt. of extract}}{\text{Wt. of sample}} \times 100.$$

34. **Rubber Hydrocarbons by Joint Rubber Insulation Committee's Method.**—Add to the flask containing the rubber residue from the alcoholic-alkali extraction sufficient water to make the total 125 ml., and then add 25 ml. of concentrated hydrochloric acid. Heat for 1 hr. at 97° to 100° C. Decant the supernatant liquid through a hardened filter paper on a Büchner funnel, 7 cm. in diameter, using suction. Wash the residue with 25 ml. of hot water and decant. (While a Büchner funnel is recommended, it is permissible to use an 11-cm. hardened filter paper with platinum cone in a 60-degree funnel.) Perform this entire treatment with water and hydrochloric acid three times. The rubber at this stage should be white and practically free from black specks of undissolved fillers; if it is not, continue the acid treatment until the black specks disappear. (If carbon is present, all the particles of rubber will be grayish, bluish, or black, depending on the form and quantity of carbon used. Black specks in light particles of rubber usually indicate the presence of lead sulfide, which must be removed to prevent the formation of lead sulfate on igniting the residue *C*.) Add 150 ml. of hot water to the flask and let stand on a steam bath or hot plate for half an hour and decant through the filter paper, repeating until the washings are free from chlorides. Transfer all the rubber in the flask to the filter paper and dry as much as possible by suction. Wash the rubber with 50 ml. of 95% alcohol, using suction. Transfer the entire residue to a weighing bottle. Dry at 95° to 100° C. for an hour, cool in a vacuum desiccator under reduced pressure, and weigh. Dry for 30 min., cool, and weigh, repeating this process until either constant weight is reached or the weight starts to increase. Let this weight be represented by *C*. Determine the ash, *E*, in a portion, *D*, of this residue, *C*, and sulfur, *H*, in the remaining portion, *G*. Also, determine the sulfur, *F*, in the ash, *E*. Perform the ash determination as described under Paragraph 23, and the sulfur determination as described under Paragraph 21. Calculations:

$$\text{Percentage of rubber hydrocarbons} = 100\frac{C}{2}\left(1 - \frac{H}{G} - \frac{E-F}{D}\right).$$

35. **Cellulose.**—Treat 0.5 g. sample of rubber with 25 ml. of freshly distilled cresol (b.p. 198° C.) on the electric hot plate for 4 hrs. at 165° C. Allow to cool and add 200 ml. of petroleum ether very slowly and with constant agitation. After the solution has settled completely, filter through a Gooch crucible and wash three times with petroleum ether. Wash very thoroughly with boiling benzene and finally with acetone. Treat the contents of the flask with hot

10% hydrochloric acid, and transfer the entire contents to the Gooch crucible with the aid of a "policeman." Continue to treat with hot 10% hydrochloric acid until the pad has been washed at least ten times. Wash the pad free from chlorides with boiling water, and run small portions of acetone through it until the filtrate is colorless. Treat with a mixture of equal parts of acetone and carbon disulfide in the same manner. Wash with alcohol and dry for 1 hr. and 30 min. at 105° C. Remove the pad from the crucible with help of a pair of sharp-pointed tweezers, using the underneath portion of the pad as a swab to clean the sides of the crucible, and place all of this material in a tared weighing bottle. Replace in the drying oven for about 10 min., cool, and weigh.

Weight of weighing bottle, pad, insoluble fillers, and cellulose
−weight of weighing bottle
=weight of pad, insoluble fillers, and cellulose.

Transfer the contents of the weighing bottle to a 50-ml. beaker and pour over it 15 ml. of acetic anhydride and 0.5 ml. of concentrated sulfuric acid, and allow to digest for at least 1 hr. on the steam bath. After the mixture has cooled thoroughly, dilute with 25 ml. of 90% acetic acid and filter through a weighed Gooch crucible. To guard against traces of the material being carried through, this filtration, as well as the ones to follow, must be very slow and only gentle suction can be used. Wash with hot 90% acetic acid until the filtrate comes through absolutely colorless, and then wash about four times more. Wash with acetone about five times. After having taken care that all of the material has been washed out of the beaker in which the acetylation took place, remove the crucible from the funnel, clean the outside thoroughly and dry for 2 hrs. at 150° C. Cool and weigh. Original weight of crucible+weight of pad, fillers and cellulose − weight of crucible after acetylation = cellulose.

$$\text{Percentage of cellulose} = \frac{\text{Cellulose}}{\text{Wt. of sample}} \times 100.$$

36. **Barium Carbonate.**—Barytes was determined by the calculation to barytes of all barium found in the sample. Obviously, if barium carbonate is present, it must be determined in order that an undue correction shall not be made. The determination is as follows: A 1-g. sample, in a porcelain boat, is placed in a combustion tube through which passes a current of carbon dioxide. The sample is ashed in the tube. After ignition and cooling in the atmosphere of carbon dioxide, the boat is removed, the residue finely ground in an agate mortar, transferred to a 250-ml. beaker, and treated with 5 to 10 g. of ammonium carbonate, 15 to 20 ml. of strong ammonia water, and about 50 ml. of distilled water. The mixture is boiled for 20 min., filtered, and the precipitate thoroughly washed to remove all soluble sulfates. The residue on the filter paper is washed back into the original beaker and about 10 ml. of glacial acetic acid with sufficient water to make the total volume about 100 ml. are added. This is heated to boiling and filtered through the same paper as before. Hydrogen sulfide is passed into the filtrate to precipitate the lead, and the solution is subsequently treated as in the determination of barytes. The final weight of barium sulfate obtained is calculated to barium carbonate.

Percentage of sulfur required to convert barium present as carbonate to sulfate

$$= \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of sample}} \times 100.$$

Calculations

37. Percentage of organic acetone extract = percentage of acetone extract (uncorrected) − percentage of free sulfur.

38. Percentage of acetone extract (corrected) = percentage of organic acetone extract − percentage of waxy hydrocarbons.

39. Percentage of waxy hydrocarbons = percentage of hydrocarbons A + percentage of hydrocarbons B.

40. Calculations for glue: Multiply the percentage of rubber as compounded (Paragraph 46) by 0.004 and 6.5 and call this value A. Subtract A from the percentage of glue (Paragraph 30) and call this value B. Substitute B for glue in Paragraph 45 in calculating the percentage of rubber hydrocarbons and then complete the calculations.

41. Percentage of sulfur as antimony trisulfide = percentage of total antimony $\times \frac{S_3}{Sb_2}$ = percentage of total antimony $\times 0.400$.

42. Percentage of total antimony as trisulfide = percentage of total antimony $\times \frac{Sb_2S_3}{Sb_2}$ = percentage of total antimony $\times 1.400$.

43. Percentage of total sulfur corrected = percentage of total sulfur − percentage of sulfur as barium sulfate − percentage of sulfur as antimony trisulfide. When barium carbonate is found, the percentage of sulfur necessary to convert it to sulfate must be added to the total sulfur (corrected).

44. Percentage of ash (corrected) = percentage of ash − percentage of sulfur in ash (+ percentage of sulfur as barium sulfate) − percentage of antimony in ash, calculated to Sb_2O_4.

45. Percentage of rubber hydrocarbon = 100 − the sum of the following percentages, except when it is determined by the J. R. I. C. method as in Paragraph 34.

Organic acetone extract	Ash, corrected
Chloroform extract	Carbon
Alcoholic-alkali extract	Glue
Total sulfur corrected	Total antimony as trisulfide

46. **Rubber as Compounded.**—Percentage of rubber hydrocarbon plus 5% of its weight is taken as "rubber as compounded," except when the sum of the percentages of the acetone extract (corrected), chloroform extract, and alcoholic-alkali extract is less than the figure represented by the arbitrary 5%, as in many high-grade compounds. Percentage of rubber as compounded is then: Percentage of rubber hydrocarbon plus the sum of the percentages of the organic acetone extract, the chloroform extract, and the alcoholic-alkali extract.

47. **Rubber by Volume.**—Percentage of rubber by volume = Percentage of rubber as compounded (Paragraph 40) $\times$ $\frac{\text{sp.gr. of compound}}{\text{0.94 (taken as the average sp.gr. of crude rubber)}}$.

48. Ratio of organic acetone extract = $\frac{\text{Percentage of organic acetone extract}}{\text{Percentage of rubber as compounded}} \times 100$.

49. Ratio of sulfur to rubber = $\frac{\text{Percentage of total sulfur, corrected}}{\text{Percentage of rubber as compounded}} \times 100$.

Statement of Results

Per cent	Per cent
Organic acetone extract	Sulfur as barium sulfate
Waxy hydrocarbons	Total antimony
Chloroform extract	Sulfur as antimony trisulfide
Alcoholic-alkali extract	Carbon
Free sulfur	Glue
Total sulfur corrected	Rubber hydrocarbon
Ash corrected	Rubber as compounded
Cellulose	Rubber by volume

Ratio of acetone extract to rubber as compounded
Ratio of sulfur to rubber as compounded
Specific gravity

Specific Gravity.—The apparent specific gravity of an unvulcanized rubber compound is almost invariably from 1% to 5% low, due to the presence of air introduced during milling, most of which escapes during vulcanization. Due to its large coefficient of expansion, rubber decreases rapidly in specific gravity with increasing temperature, and raw rubber undergoes a change of state and sudden drop in sp.gr. from approximately 0.93 to 0.91 at around 30° C., which is only slowly reversible on cooling.[7]

For ordinary purposes, it is sufficiently accurate to suspend a small sample from the beam of a balance of a Young's Gravitometer, and after balancing, wet the surface by raising a beaker of alcohol under it, remove the alcohol by use of a beaker of wash water, and weigh suspended in distilled water as usual, thus avoiding air bubbles.

For factory control purposes, use of solutions of $CaCl_2$ or $ZnCl_2$ of proper strength permits rapid checking of samples between predetermined limits. Thus a piece of stock which should be of 1.12 sp.gr. will float on a solution of 1.13 sp.gr. and sink in a solution of 1.11 sp.gr.

Extracts.—Hard asphalt hydrocarbon (mineral rubber), mineral oil, stearic acid, palm oil, pine tar oil, hardwood pitch, etc., are frequently added as softeners or for other specific purposes. The analytical estimation of these soft-

[7] Pickles, India Rubber Jour. **67**, 17 (1924).

eners is not an exact matter. On the other hand, an approximation is all that is usually required.

Plantation rubbers yield acetone extracts usually between 2.0% and 3.5%, while various grades of wild rubbers give extracts up to 10.0%, or even higher for resinous grades. These extracts are usually of a soft consistency, and until the use of added softeners became common, wild rubbers were largely used for softening purposes.

Reclaimed rubber is variable in composition, depending on the source, but that made from whole tires usually falls within the following limits:

Specific Gravity	1.16 – 1.24
Moisture, max.	1.0%
Alkalinity, max., 4 hr. ext.	0.10%
Acetone Ext.	7.0% –12.0%
Chloroform Ext.	10.0% –18.0%
Alcoholic KOH Ext.	1.0% – 2.0%
Total S	3.0% – 4.0%
Free Carbon	3.5% – 7.5%
Ash	18.0% –35.0%

Added softeners are partially extracted from a cured stock by acetone, and subsequent extraction with chloroform removes still more, but there is always an appreciable amount of the softener which is not extracted, depending on the type of softener, type of compound, cure, etc. Mineral rubbers for instance, vary greatly, some coloring the acetone extract dark brown, and others not at all, some carrying a large amount of sulfur and consequently combining with little additional, while others tend to "hog" sulfur during the cure. Very little analytical work is available to show the extraction under definite conditions. The following is an example of the extraction of 3.0% of softener from a well cured "pure gum" compound carrying 3.5% sulfur.

Softener	Recovered in Acet. Ext.	In $CHCl_3$ Ext.	Not Recovered
Mineral Rubber	44.3%	28.7%	27.0%
Hardwood Pitch	46.3	10.7	43.0
Pine Tar Oil	68.0	14.0	18.0
Mineral Oil	70.0	4.4	25.6

Saponification of the acetone extract gives some idea of the percentage of mineral oil softeners present, but is seldom resorted to. Acetone extracts can be checked to within 2% of the extract, and $CHCl_3$ extracts to within 4%.

Alcoholic KOH extract is run only when the presence of oil substitute (factice) is known or suspected. It removes about 50% of the substitute, and must be corrected for an extraction of about 0.5% on the rubber, and 1.5% of any reclaim present. When substitute is present, the acetone extract must be corrected for about 10% of the substitute in the case of black or brown substitute, this correction being largely unvulcanized oil.

Sulfur.—The sulfur present in a rubber compound comes from two sources, (1) sulfur added for vulcanization purposes, and (2) sulfur present in the compounding ingredients.

The latter may be a considerable percentage of the total sulfur, as the following table of the per cent usually found in some of the common ingredients will show.

Whole Tire Reclaim	3.5%
Reclaimed Friction	1.0
Mineral Rubber	1.0– 7.5
Hardwood Pitch	nil
Lithopone	9.5
Golden Antimony	20.0–40.0
Ultramarine Blue	10.0
Mercaptobenzothiazole	35.0
Thiocarbanilid	16.0
Diphenylguanidine	nil

The only one of these affecting the free sulfur determination is golden antimony. This comes in a number of grades, the most common being that containing 40–43% of coprecipitated $CaSO_4$ and 15–17% of free S. Most accelerators are somewhat soluble in hot acetone, and their S would appear as free S in an uncured stock, but during the cure these are largely decomposed, and any residual effect on free S is negligible.

During vulcanization, sulfur combines in four ways, (1) with the rubber hydrocarbon, (2) with the natural resins and proteins, (3) with softeners if present, and (4) with inorganic oxides to form sulfides such as ZnS. This has been discussed by Kelly in several papers [8] and methods of separation given. The ordinary figure for combined sulfur (corrected total sulfur-free sulfur) includes all of these forms, and also the sulfur from various compounding ingredients as noted above. When interpreted in connection with the formula of a compound and the processing to which it has been subjected, it is an excellent indication of the state of vulcanization. The percentage of combined sulfur (CS) divided by the percentage of rubber present in a compound, gives the coefficient of vulcanization (VC). Plotting either VC or CS against time of cure gives a smooth curve for any given temperature conditions. It is thus possible to take a sample from any point in a finished article, and by determining its VC, estimate the equivalent cure. It should be remembered however, that in the case of a tire or other complex article in which several stocks are cured in contact with each other, migration of sulfur from a high sulfur stock to one of lower sulfur content (on the rubber) is liable to occur, and also that sulfur tends to migrate in the direction of the source of heat.

Free sulfur is at times a useful indication of the "non-blooming" characteristics of a stock, usually less than 1.0% FS on the rubber being necessary to prevent sulfur "bloom."

Sulfur determinations have a tendency to run slightly high, usually not over 0.10%. Duplicates by extremely careful work can be made to check within 0.04% S, but on ordinary rubber work, any variation not over 0.10% is satisfactory checking.

Ash.—An ash determination is only an approximation of the amount of inorganic fillers in a stock, as it is affected by several factors. The various clays, asbestine, lime, etc., carry considerable percentages of combined water which is volatilized over a range of temperature. Whiting tends to lose CO_2

[8] Ind. Eng. Chem. **12**, 875; **14**, 196; **16**, 148.

unless very carefully handled. During the ignition, much of the sulfur present combines with any zinc oxide, lime, magnesia or litharge to form sulfates. If the sample is allowed to catch fire, zinc oxide will be reduced and volatilized. In practice, ash serves as a check on the subsequent analysis of the ash, and sometimes itself gives sufficient information on the leading of a stock.

Analysis of Ash.—In addition to the determinations of sulfur, barium sulfate and antimony given in the standard methods, it is frequently necessary to further analyze the ash to secure an idea of the fillers and inorganic accelerators present in the sample. SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, PbO and ZnO are usually determined, but as these occur in many fillers in varying proportions, some judgment is necessary for the proper interpretation of results, and microscopical methods are of considerable aid in determining the fillers present.

Particularly in the field of cheap inert fillers, the compounder's choice is often affected by the location of the factory and the materials most easily available, as similar stocks can frequently be made with widely varying compositions.

The following table shows the approximate percentages found in some commercial compounding ingredients:

Asbestine—MgO 25%, SiO_2 65%, Al_2O_3 3.5%, CaO 1.5%, Ign. Loss 5.0%.
Barytes—$BaSO_4$ 90–95%.
Dixie Clay—SiO_2 46%, R_2O_3 39%, CaO trace, MgO trace, Ign. Loss 15%.
Lead Oleate—PbO 25–30%.
Lime—$Ca(OH)_2$ 91%.
Lithopone—ZnO 29%, $BaSO_4$ 71%.
Mag. Carb.—MgO 42%, Ign. Loss 50%.
Mag. Usta—MgO 87%, CaO 2.5%, SiO_2 and R_2O_3 4.0%, Ign. Loss 6%.
Whiting (pptd.)—CaO 50%, MgO 3%, SiO_2 and R_2O_3 5%, Ign. Loss 40%.

Free Carbon.—The direct determination of free carbon is quite accurate. In addition to carbon black, the most used reinforcing filler, small percentages of free carbon may come from any mineral rubber or hardwood pitch present, but these are usually neglected.

Glue.—The presence of as little as 0.9% glue can be detected qualitatively, but of late years, the use of glue in rubber compounds has become quite rare.

Calculation of the Probable Composition of a Stock.—The experienced compounder will draw heavily on his knowledge of the compounding ingredients available and suitable to use in a stock giving properties of the sample, in calculating its probable composition, but the following will give an idea of general procedure.

1. From the analysis of the ash, estimate the amounts of fillers and inorganic accelerators used, allowing 15% ignition loss for clays, and using data such as general appearance of the stock, state of cure, color, etc., to aid in judging the amounts of CaO, MgO, and PbO used, if any.

2. Estimate carbon black, glue, and substitutes if any, from their special analyses.

3. Estimate rubber hydrocarbon by difference. Subtract 3.0% of this from the combined sulfur, and see if the use of reclaim is indicated. The odor of the stock is also often characteristic in connection with either reclaim or softeners such as pine tar oil. If much CS is left over, figure it as 3.5% of reclaim, and check this indicated reclaim content with the other extracts and ash to see if it seems reasonable.

4. Subtract 10% of the estimated reclaim and 3.5% of the estimated rubber content from the acetone extract, and estimate the kind and amount of softeners used from the remainder, taking into account the character of the extracts, and correcting the chloroform extract if necessary for the effect of the reclaim present.

5. Figure the sulfur used as total sulfur less 3.5% of the reclaim and 6.0% of any mineral rubber present.

6. Calculate the specific gravity of the stock from the probable composition, and compare with the actual specific gravity, which should be within 0.02, except in the case of compounds containing large amounts of softeners or sulfur, with which the actual gravity is usually several points higher than the theoretical.

ANALYSIS OF RAW MATERIALS

Raw Rubber.—All but a very small percentage of the rubber used in the United States is plantation grown, and appears upon the market quite clean and dry, and graded (by appearance and history) according to standards established by the Rubber Exchange of New York. Except for research purposes, the chemical laboratory is seldom called on to determine more than moisture, acetone extract and ash. The factory, however, is interested in the rate of cure and physical properties with given formulae, which vary widely with rubber of identical appearance. For control purposes, it is common to blend at least three lots of rubber together on mixing mills, and evaluate the blend by means of physical tests on experimental batches, the formulae used varying with the factory and the use to which the rubber is to be put. Methods for special analytical determinations are given in the previous chapter. For data on the chemistry and structure of hevea rubber, see Dinsmore, Ind. Eng. Chem. **18**, 1140–5 (1926), and Fisher, Chemical Reviews, **VII**, 1 (Mar. 1930).

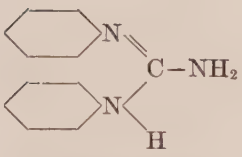
Reclaim —Reclaimed rubber is classified according to the type of rubber scrap from which it was prepared, and is subjected when required, to the same chemical examination as a rubber compound, with particular emphasis on specific gravity, moisture, alkalinity, acetone extract and ash. These tests however, are mainly useful in control of material of known source and type, and any new material requires physical testing, both alone and in the type of compound where it is to be used, and also factory tests in actual production compounds to determine the effect on factory handling conditions.

Accelerators and Antioxidants.—A very considerable number of substances, mostly organic, has come into use in recent years as additions to rubber compounds to accelerate the rate of vulcanization, or to retard the rate of deterioration after vulcanization. A few of these are of definite composition that permits simple tests for purity. Most, however, are complex, and require extended physical tests for their evaluation, and are consequently sold chiefly without test on the strength of their manufacturer's reputation. Data with

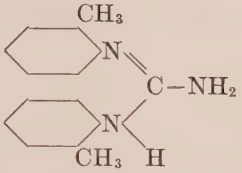
respect to the classification of accelerators have been published by Dinsmore and Vogt, Rubber Chem. and Tech., **1**, 410 (1928), and by Martin and Thiollet, Rubber Chem. and Tech., **2**, 356 (1929) and **3**, 38 (1930). See also Callan and Strafford, Chem. and Ind., Jan. 4, 1924. The following common accelerators are usually subjected to chemical specifications as shown below.

Guanidines

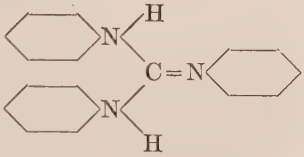
Formulae.—



Diphenylguanidine (DPG)



Diorthotolylguanidine (DOTG)



Triphenylguanidine (TPG)

Moisture.—Max. 0.5%. Dry to constant weight at 105° C.

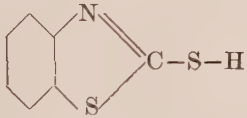
Ash.—Max. 0.5%. Ash one gram sample and weigh residue.

Purity.—Min. 97.0%. Dissolve one gram sample in 25 ml. alcohol, titrate with 0.1 N alcoholic HCl using bromphenol-blue indicator. 1 ml. 0.1 N HCl = .0211 g. DPG, .0239 g. DOTG, .0287 g. TPG.

Fineness.—100% through 100 mesh, min. 99% through 200 mesh. Use a camel's hair brush lightly to assist in sifting.

Mercaptobenzothiazole

Formula.—



Trade name, "Captax."

Moisture, Ash and Fineness, as above.

Purity.—Min. 90.0%. Dissolve one-half gram sample in 25 ml. alcohol and titrate with 0.1 N alcoholic NaOH, using phenolphthalein indicator. 1 ml. 0.1 N NaOH = .0168 g. mercaptobenzothiazole.

Softeners

Softeners constitute an important class of rubber compounding ingredients, as in addition to modifying the properties of the vulcanized compound, and in most cases reducing the cost, they greatly affect the properties before vulcanization and often make possible large savings in processing. A great many materials are used, including petroleum products such as refined lubricating oils, petrolatums, paraffin, and blown asphalts (mineral rubber), vegetable oils such as cottonseed oil, palm oil, and castor oil, wood distillation products such as pine tar, pine tar oil and hardwood pitch, resins such as rosin, glycerol ester, cumar, dammar and shellac, and fatty acids such as stearic, oleic and lauric and their zinc salts.

The most essential feature from the compounder's standpoint is the uniformity of the material selected, and ordinary tests for melting point, viscosity, etc., appropriate to the product are applied, the only features peculiar to rubber being that copper and manganese must be absent, on account of the very deleterious effect of even minute traces in rubber compounds, and alkalinity or mineral acidity must be absent on account of the effect on the rate of vulcanization.

Fillers and Reinforcing Agents

Reinforcing agents such as carbon black, zinc oxide, light magnesium carbonate, and certain processed clays; color pigments such as iron oxide, chrome green, golden antimony, and various dyes and lakes, and mineral fillers such as whiting, barytes, clay and asbestine, are widely used in rubber compounding for their effects on the cost and physical properties of the stocks.

In this connection, it may be mentioned that the custom has arisen in American rubber factories of calling many compounding ingredients "pigments," regardless of whether they are colored or not. This is chiefly due to the practice of writing formulae in code, a certain "pigment number" representing a given ingredient, and the term even being extended to softeners such as pine tar and solvents such as benzol.

On account of the great effect of particle shape, size and surface condition, all material from new sources requires testing in actual compounds before it can be approved for use, but for control purposes on material from known sources, customary tests for purity and uniformity can be applied. All materials should pass 100% through 100 mesh, this in the case of reinforcing pigments being merely to detect the presence of any lumps, as the individual particles are far finer than any screening test can grade. On carload shipments, the screening test should be made on a representative sample of 200 pounds to detect stray contamination. All materials should be dry, free from copper and manganese, free from alkalinity and acidity, and except for lead compounds used as such, free from lead. Other properties of interest to the rubber compounder include specific gravity, particle shape and size, heat conductivity, specific heat, reactivity with sulfur, volatile matter at curing temperatures, and tendency to agglomerate during milling. A few special tests follow.

Carbon Black.—Simultaneously determine moisture by heating a sample one hour in an electric oven at 105° C., and total volatile by heating a one gram sample in a platinum crucible with capsule cover in an electric furnace for seven minutes at 955° C. Difference is volatile matter, which in excess of 5.5%–6.0% has been shown to lower the quality of the black materially for rubber purposes.

Any black of different type from standard will show difference in covering power, determined as follows: take sample of 0.050 g. each of standard black and of sample to be tested, and place side by side on a clean glass plate. To each, add 2.00 g. standard zinc oxide and 30 drops of pure raw linseed oil. Mix each by rubbing with a spatula until the resulting paste is smooth and free from streaks. Compare colors by placing small portions of each on a microscope slide and pressing with a second slide. Add additional zinc oxide if necessary from a weighing bottle until the pastes show exactly the same color.

$$\frac{\text{Wt. ZnO for standard}}{\text{Wt. ZnO for sample}} = \text{covering power.}$$

Zinc Oxide.—Test for covering power, using standard carbon black as above. Determine sulfates by dissolving 2 grams in 50 ml. water and 10 ml. concentrated HCl, adding 5 ml. Br water, boiling off excess Br, and precipitating with $BaCl_2$. Max. 0.20% SO_3. Determine lead by dissolving 5 g. in 60 ml. 1 : 1 HNO_3, diluting to 400 ml., and throwing out PbO_2 electrolytically. Max. 0.20% PbO. Compare particle size and shape by grinding a few mg. in turpentine, mounting on a slide to form a very thin film, and comparing under the microscope with a standard sample.

Color Pigments.—Compare color and fineness by grinding 0.050 g. to 0.100 g. sample into 2.0 g. ZnO and linseed oil as in covering power test.

Solvents.—On account of their lower price range, solvents derived from petroleum are chiefly used in this country for making rubber cements, other solvents such as benzol, xylol, carbon bisulfide and carbon tetrachloride being used only for special purposes. The petroleum solvents are held to very close distillation specifications to control the rates of drying of the rubber cements. Low boiling fractions are to be avoided as much as high boiling fractions, as they cause greater fire hazard and large loss of solvent during mixing and handling. Specifications usually call for no residue on evaporation at room temperatures, no acidity to methyl orange, sweet odor, negative doctor test, and color not over 30 Saybolt. Typical distillation specifications for rubber maker's naptha, using the standard A. S. T. M. method, are as follows:

IBP	min. 52° C.	min. 73° C.
10%	min. 67	min. 82
20	min. 72	min. 84
40	min. 81	min. 88
60	max. 90	max. 93
80	max. 105	max. 100
DP	max. 144	max. 128

SLAG ANALYSIS [1]

The slags made in metallurgical operations consist of complex mixtures and solid solutions of silicates, oxides, aluminates, fluorides and many other compounds. In the molten condition some of these components are probably in igneous solution in each other, their exact composition and the nature of their association depending upon the state of equilibrium at the time the slags were produced. The composition of slags is important both because of its influence upon furnace operations and because of its effects upon the character of the metallic products. For these reasons it is necessary to make frequent slag analyses in all metallurgical plants.

In iron blast-furnace slags the principal constituents are silica, alumina, lime and magnesia, with small amounts of iron oxide, manganese oxide, calcium sulfide and phosphoric acid. Titanium oxide is also frequently present. In modern blast-furnace practice, which involves the use of high lime slags, in order to keep sulfur out of the iron, the percentage of lime and sulfur in the slags is closely watched. In open-hearth furnace slags the amount of phosphorus may be high enough to warrant the sale of the slag as fertilizer.

Lead blast-furnace slags consist mainly of silica, iron oxide, manganese oxide, lime, alumina and zinc oxide, with small percentages of magnesia, barium oxide, lead, copper and sulfur. Of these the most important to the metallurgist are silica, iron oxide, lime, zinc oxide and lead, and determinations of them must be made at least once a day. The other components are determined less frequently. In some of the Mexican lead-smelting plants calcium fluoride occurs in the blast-furnace slags. The lime combined as fluoride is determined separately, as it is not available for the saturation of silica.

Copper slags are made up mainly of silica, iron oxide, lime and alumina. The manganese oxide and the zinc oxide are usually less than in lead slags. The silica and alumina, however, are generally higher. This is especially true in the case of reverberatory slags, in which a greater viscosity can be permitted. The percentage of copper is quite important as it measures the chief source of loss of that metal. The percentage of copper in the slag is usually about one hundredth of that in the matte. The amount of lime in copper slags varies a great deal more than it does in lead slags, as it is of less importance in influencing the metallurgical results. In converter slags the copper may amount to several per cent, and the slag then becomes an important by-product.

Composition of Slags

Blast-Furnace Slags.—SiO_2 = 35 to 45%; FeO = 0.2 to 0.5%; CaO = 32 to 46%; Al_2O_3 = 14 to 17%; MgO = 1.0 to 1.5%; MnO_2 = trace to 0.1%; S = 1.5 to 2.0%; P_2O_5 = 0.01 to 0.96%.

Lead Blast-Furnace Slags.—SiO_2 = 36.7%; FeO = 29.5%; CaO = 20.9%; Al_2O_3 = 3.16%; MgO = 1.69%; MnO = 0.91%; S = 0.75%; BaO = 0.54%; ZnO = 4.19%; Pb = 1.38%; Cu = 0.10%; Au = 0.001%; Ag = 0.70%.

[1] By Wilfred W. Scott.

Average of one year's analyses on representative samples.

Copper Blast-Furnace Slags.—SiO_2 = 23 to 49%; Fe(MnO) = 2.5 to 57%; Ca(MgO) = 2.5 to 25%; Al_2O_3 = 1.5 to 18%; ZnO = nil to 23%; Cu = 0.15 to 1.1%; S = nil to 1.5%.

Decomposition of the Sample and Analysis

General Reverberatory Slag.—Usually 0.5 gram of the finely ground slag is taken for a determination, a larger amount when the constituents sought are present in very small amount. The material placed in a platinum crucible is fused with 5 to 6 grams of Na_2CO_3 at red heat (muffle furnace, if possible) for 10 minutes. The mass is cooled on the side of the crucible, and the fusion dissolved in a casserole by adding an excess of HCl, followed by a few ml. of HNO_3. The solution is evaporated to dryness and the residue baked. The mass is taken up with dilute HCl. Silica remains as a residue and is filtered off and determined. The metals are determined in the filtrate.

Chilled Blast Furnace Slag.—The sudden chilling of the molten slag by dropping into water causes a physical change in the material which enables a decomposition by means of acids without resort to fusion, as given above.

About 0.5 gram of the finely ground chilled slag in a small casserole is moistened with water and about 3 ml. of concentrated HCl added. All lumps are broken up by stirring with a glass rod until a smooth jelly results. A few drops of HNO_3 are added to oxidize the iron and the jelly is worked up around the sides of the casserole in an even layer to the height of about ½ inch. (This permits rapid dehydration of the silica and reduces loss by "spitting.") The acids are expelled by evaporation and the residue gently baked. (If the temperature is too high, some alumina will combine with the silica and give high results for SiO_2.) After cooling, about 20 ml. of concentrated HCl are added and the mixture boiled for a few minutes, then diluted with an equal volume of hot water and filtered hot. SiO_2 remains as a residue, the metals are in solution.

Silica.—The residue obtained from the decomposition is washed with hot water until free from chlorides, the washings being added to the main filtrate. The residue and filter are ignited, then cooled and weighed as SiO_2.

Note.—Should barium be present, as is the case with many lead slags, nitric acid is omitted in the decomposition, as this would cause contamination of the silica with barium sulfate. If nitric acid is used, it is advisable to obtain the silica by difference, by first weighing the residue. This is placed in a weighed platinum dish, then treated with hydrofluoric acid and a few drops of sulfuric acid. The solution is evaporated, all the acids and the silica being expelled (as silicon fluoride). Any remaining residue is weighed and subtracted from the first weight obtained. The loss represents the SiO_2.

Copper slags carrying 40 to 45% of SiO_2 are more troublesome than those with 35 to 37% of SiO_2 in regard to alumina uniting with the silica during dehydration.

Lime.—(In presence of iron oxide and alumina) Ammonia is added to the filtrate from silica and then oxalic acid little by little until the precipitated iron and aluminum hydroxides just dissolve. The solution is again made ammoniacal and oxalic acid again added to dissolve iron. The solution should appear a light apple-green color. It is now boiled for a few minutes and the precipitated calcium filtered off and washed with hot water until free from oxalic acid, six or seven times being generally sufficient.

The filter containing the calcium oxalate is dropped in a beaker, 150 ml. of hot water added together with 15 ml. of (1 : 1) H_2SO_4 and the oxalic acid titrated with standard potassium permanganate.

1 ml. of 0.1 N $KMnO_4$ = 0.0028 gram of CaO.

The Fe value of $KMnO_4$ multiplied by 0.5 = CaO value.

NOTES.—If preferred, iron and aluminum may be precipitated as hydroxides, and filtered off, calcium being determined in the filtrate. It is advisable to redissolve the precipitate to recover any occluded lime and again precipitate the hydroxides with ammonia, the filtrate being combined with the main filtrate.

In place of titrating the oxalate of lime, it may be ignited and the residue weighed directly as CaO.

If oxalic acid is added in the form of a fine powder instead of a solution, the calcium precipitates in a much more granular form and requires less boiling before filtering.

Iron.—(In presence of silica) Half a gram or more of the finely ground chilled slag in a beaker is treated with 50 ml. of boiling water, the particles stirred up and kept in suspension and about 25 ml. of concentrated HCl added. The solution is boiled until clear. (If coke dust is present it will still be evident, but may be neglected.) Stannous chloride solution is added, drop by drop, until the iron is reduced (solution becomes colorless) and 2–3 drops excess added. The solution is cooled by placing the beaker in cold water. Mercuric chloride, $HgCl_2$, solution is added to precipitate the excess of stannous chloride.

The iron is determined by titration with standard potassium dichromate, using ferricyanide indicator on a spot plate. See subject in the chapter on Iron. Report as FeO.

1 ml. of 0.1 N $K_2Cr_2O_7$ = 0.00558 g. of Fe, 0.00719 g. of FeO,
Fe × 1.2865 = FeO.

NOTE.—The iron may be precipitated as hydroxide, then dissolved in dilute H_2SO_4, the solution reduced by boiling with test lead or reduced in cold solution with zinc and the solution titrated with standard potassium permanganate. This method is frequently preferred where previous fusion to decompose the ore has been required. Lime may be determined in the filtrate from iron.

Determination of Other Constituents in Slags

Alumina: *Phosphate Method.*—The filtrate from the silica determination is diluted to about 400 ml. with cold water and 30 ml. of 10% ammonium phosphate added. Dilute ammonia water is added until a slight permanent precipitate forms.

1.5 ml. of concentrated HCl is added and 40 ml. of 20% solution of $Na_2S_2O_3$ and the mixture boiled for about two or three minutes. 15 ml. of 20% ammonium acetate and 6 ml. of concentrated acetic acid are added and the boiling continued for about 15 minutes.

The precipitate is allowed to settle for 15–20 minutes, the clear solution decanted through a filter and finally the aluminum phosphate filtered and washed. (The presence of the acetate makes the compound more granular.) 10 washings with hot water are sufficient.

The precipitate is dried, ignited and weighed as $AlPO_4$.

The precipitate contains 41.85% Al_2O_3.

NOTE.—The slag may be decomposed by treating 0.5 gram in a platinum dish with 5 ml. HNO_3, 6 ml. of HF and about 2 ml. of (1 : 1) H_2SO_4. The sample is taken to strong fumes of SO_3, then cooled and 10 ml. of HCl added and the mixture boiled. Alumina and iron may now be precipitated as hydroxides, and filtered off and washed. After dissolving in HCl, precipitate $AlPO_4$ as in the method above.

Manganese.—Half a gram of the slag is placed in a beaker and about 50 ml. of water added, the solution stirred until the material is in suspension and about 15 ml. of HCl added, followed by 5 ml. of HNO_3, and the solution boiled until most of the chlorine has been expelled.

Hot water is added to make up to a volume of about 100 ml. The iron is now precipitated by adding ZnO emulsion until the acid is neutralized and an excess of ZnO forms on the bottom of the beaker.

The solution is boiled for a few minutes and the manganese titrated while the solution is still hot (in presence of the precipitate) with standard potassium permanganate.

The end-point is best seen by allowing the precipitate to settle slightly and observing the clear upper stratum of the liquid.

1 ml. of 0.1 N $KMnO_4 = 0.00165$ g. of Mn.

The lime value of the $KMnO_4 \times 0.588 = Mn$.

NOTE.—In place of the method given above consult the chapter on Manganese for the volumetric oxalic acid method.

Zinc.—To 0.5 gram (1 gram if zinc is low) of the sample in a casserole is added 3 ml. of water, 5 ml. of HCl and 2 ml. of HNO_3. When the SiO_2 is completely gelatinized, about 4 grams of NH_4Cl is stirred in.

The sample is dehydrated only until the residue crumbles easily as baking is liable to volatilize some zinc as chloride. About 30 ml. of hot water are added and the solution brought to boiling, filtered and the residue washed with hot water.

To the filtrate ammonium persulfate and bromine are added, the amount being governed by the manganese present, *i.e.*, 0.03 g. of ammonium persulfate and 10 ml. bromine for every 0.01 g. of Mn in solution. Ammonia is added in slight excess, the solution boiled about 2 minutes, filtered, and the residue, MnO_2, etc., washed. (It is advisable to redissolve the precipitate in a little dilute HCl and again precipitate with persulfate and bromine, adding the filtrate to the main filtrate.)

The solution is just neutralized with HCl and 5 ml. excess added, followed by 2 grams of test lead. The solution is boiled about 15 minutes.

About 8–10 ml. of HCl are added, the solution heated to about 60° C. and the potassium ferrocyanide added. When the titration is almost completed, the bluish-white color of the precipitate changes to nearly pure white.

If the ferrocyanide is made up by adding 21.63 grams of potassium ferrocyanide per liter of solution, 1 ml. will equal very nearly 0.005 gram of Zn. Consult chapter on Zinc.

In place of the above method the rapid method given in the chapter on Zinc may be followed.

Magnesia.—0.5 gram or more of the finely ground chilled slag, placed in a casserole, is moistened with water, 5 ml. of HCl and a few drops of HNO_3

added. The acids after reacting with the slag are evaporated off and the silica dehydrated. The residue is taken up with 15 ml. of HCl and about 30 ml. of water, and boiled.

Silica is filtered off and washed.

The filtrate is made slightly alkaline with ammonia, 8 ml. of $(NH_4)_2S$ and 1 gram of $(NH_4)_2CO_3$ added and the solution boiled for a few minutes, the precipitate then filtered off and washed several times with water containing a little $(NH_4)_2S$.

The filtrate is made slightly acid with HCl and boiled down to about 50 ml. The precipitated sulfur is filtered off and the filter washed. If the solution is cloudy, it is cleared by adding bromine water and boiling.

Ammonia is now added, and a small amount of ammonium oxalate to remove any CaO still remaining; after boiling, the oxalate of calcium ("lime") is filtered off and washed.

Magnesia is now precipitated in the filtrate by addition of Na_2HPO_4 or another alkali phosphate, and the magnesium ammonium phosphate filtered off, washed with 2% ammonium nitrate solution, ignited and weighed as $Mg_2P_2O_7$. Consult the chapter on Magnesium.

$$Mg_2P_2O_7 \times 0.3621 = MgO.$$

Copper: ***Colorimetric Method with Ammonia.***—The percentage of copper normally present in blast furnace slags should not exceed 0.3%. Converter slags may contain as much as 2.5% copper. The colorimetric method is especially adapted for this determination owing to its simplicity and speed.

Slags which have been "chilled" are *readily* decomposed by HCl. Stirring constantly during the acid action and diluting as soon as decomposition is complete prevents the separation of gelatinous silica and hastens the solution of copper.

Procedure: ***Color Standards.***—0.2 gram of pure copper foil is dissolved in 20 ml. of 1 : 1 HNO_3 in a covered beaker, warming gently. After evaporating down to about 10 ml., the solution diluted to 50 ml. is transferred to a graduated liter flask, 200 ml. of ammonium hydroxide added and the solution diluted to 1000 ml.

5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ml. portions are taken and placed in 100-ml. Nessler colorimetric tubes. (In place of the tubes clear white glass bottles of about 150 ml. capacity may be used.) The volume of each solution is diluted to 100 ml. with 1 : 5 ammonium hydroxide.

If a colorimeter is available, a standard is taken that corresponds to that of the sample as prepared according to directions below and comparisons made by viewing the solutions through the depth of solutions adjusted to give the same intensity of color.

Preparation of the Sample.—Two grams of the finely crushed sample (100-mesh) is treated in a beaker with 10 ml. of water to thoroughly moisten the powder, 10 ml. of concentrated HCl are added and the mixture stirred, warming gently until the undissolved residue becomes flocculent, remaining in suspension.

About 90 ml. of H_2S water are added or the same volume of water and H_2S gas passed in until the solution is saturated. The solution is warmed gently

until the copper sulfide coagulates. The precipitate is filtered through a small filter (a Witt filter is satisfactory) and washed with H_2S water.

The sulfide is now dissolved in 5 ml. concentrated HNO_3 (in the beaker in which the CuS was precipitated), 30 ml. 1 : 5 NH_4OH solution are added, the solution filtered through a second filter, and this washed with 1 : 5 ammonia reagent.

The copper solution is transferred to a Nessler tube (bottle or colorimeter tube as the case may require) and comparison made with a standard, the solution being made up to 100 ml. with 1 : 5 NH_4OH.

Electrolytic and Iodide Method for Copper

For extreme accuracy the electrolytic or iodide methods are recommended. Details of these methods may be found in the chapter on Copper. See also the chapter on Fire Assay Methods by I. A. Palmer.

Lead.—The determination of lead is frequently required in slags. Slags high in silica are apt to contain lead in appreciable quantities, probably combined as silicate. The decomposition of the slag by treatment with HF as given in the footnote on page 2021 is recommended.

The determination of lead in slag does not differ materially from its determination in ores. Reference is made to the chapter on Lead for its estimation.

Other Constituents.—The determination of barium, titanium, sulfur, phosphorus, chromium, cobalt, nickel, alkalies, etc., is occasionally necessary. The procedures for these determinations may be found in the chapters dealing with the elements in question.[1]

[1] The introduction to this section "Slag Analysis" was written by Prof. I. A. Palmer, Department of Metallurgy, Colorado School of Mines.

A number of the procedures appearing in this chapter on slag analysis are standard methods used at the Washoe Smelter of the Anaconda Copper Mining Company and are procedures originally suggested by Professor H. W. Thomson, Department of Mining, The University of British Columbia.

METHODS FOR ANALYSIS OF SOAPS AND SOAP PRODUCTS [1]

Soap is the term generally applied to the alkaline salts of the non-volatile fatty acids. From a scientific viewpoint, all metallic salts of fatty acids are soaps; most of them are, however, insoluble in water and, therefore, not commonly used as cleaners. Commercial soaps are made by saponification of glycerides of fatty acids with sodium or potassium hydroxide, or by saponification of fatty acids with sodium or potassium carbonate. Various manufacturing methods are employed, but the two most common are the " cold process " and " boiled process." In the " cold process " the fat and alkali are combined in the cold, and since no salt is added to " grain out " the soap, it contains all of the impurities of the fat and alkali, and all the glycerin. " Boiled soaps " are made from fat by boiling in a kettle with sodium hydroxide or carbonate. Salt is added to " grain out " the soap, which separates the soap from most of the glycerin and impurities.

To soaps made by either of the above processes may be added various ingredients to obtain certain characteristics and qualities desirable from a viewpoint of appearance and of detergency. Perfumes, coloring matter, and medicants are added to toilet soaps; transparent soap is a combination of soap, alcohol, sugar, and glycerin. Some soaps may contain fillers added to impart special characteristics. A few of these are colloidal clay, pumice, oatmeal, bran, sawdust, milk, ground corn, blood albumin, gliadin, cellulose, etc. Medicated soaps may contain carbolic acid, thymol, petroleum, vaseline, camphor, gelatin, iodides, chlorides, zinc stearate, zinc oxide, and mercuro-compounds.

From this brief description it can be seen that a soap received in a laboratory may contain any of the various constituents mentioned. The following methods include only those commonly encountered in soap analysis. When analyses for fillers are desired other than those described, the usual methods for such materials are applicable.

In compiling these methods, in many cases the standard methods for the sampling and analysis of commercial soap and soap products of the American Chemical Society [2] and of the American Oil Chemists' Society [3] are used, and acknowledgment is given. In some cases the A. C. S.—A. O. C. S. methods are modified or replaced by methods which have been developed for soap works laboratories where a large number of samples are handled daily for control purposes, so that methods must be rapid as well as accurate. For sampling of

[1] Compiled by the Chemical Division of the Procter and Gamble Co. Through the courtesy of the Company and C. P. Long. The Methods approved by the A. C. S. and A. O. C. S. Committees on the Analysis of Soaps and Soap Products have been incorporated.

[2] Standard Methods for Sampling and Analysis of Commercial Soaps and Soap Products, J. Ind. Eng. Chem., **14**, 1159 (1922); Ind. Eng. Chem., Anal. Ed. **9**, 2 (1937).

[3] Standard Methods for Sampling and Analysis of Commercial Soaps and Soap Products, Oil and Soap, **11**, 90 (1934).

shipments in commercial transactions, the methods prescribed by the two societies referred to should be used.

PREPARATION OF SAMPLES FOR ANALYSIS

The instructions follow A. C. S.[2]—A. O. C. S.[3] methods in general detail.

Cakes or Bars

Samples on which an entire analysis is to be made should be run through an ordinary food chopper. If the sample cannot be easily disintegrated and mixed, it should be quartered by cutting at right angles in the center and portions from all freshly cut surfaces shaved off with a knife, portions of these shavings being used for analysis. Freshly stamped bars obtained in plant control may be sampled with a cork borer of convenient diameter. Both ends of the sample plug should be cut off and rejected. The samples should be preserved in air-tight containers in a cool place. Excessive exposure to the air and handling with the hands should be avoided as much as possible.

Powders, Flakes, and Chips

Samples in cartons should be removed and thoroughly mixed on an oil cloth. The sample should be reduced if necessary by quartering or passing through a riffle. It is then placed in airtight containers. Quart Mason jars are convenient. Flakes should be broken up as much as possible with a knife or chopper. Containers should be completely filled with the sample. When removing portions for analysis the entire sample should be mixed in the container with a spatula.

Paste Soap Products

The sample should be removed from its original container, thoroughly kneaded and mixed well. Portions for analysis should be weighed quickly and the remainder kept in an airtight container in a cool place.

Liquid Soap

The sample should be mixed carefully with a spatula or spoon. Shaking or any action to form suds should be avoided. Unused portions should be kept in air-tight glass containers.

METHODS OF ANALYSIS

When a determination shows non-conformity with specifications, a duplicate should be run. If the sum of all the constituents is not reasonably close to 100%, the entire analysis should be re-run, beginning with moisture and volatile matter and anhydrous soap. In case of heavily silicated soaps, some moisture will be retained by the silicate, and when appreciable amounts of glycerin or solvents are present, the moisture and volatile value will be high. These facts should be taken into consideration when interpreting final results.

Moisture and Volatile Matter (Oven Method)

Weigh a 5±.01 gram sample rapidly in a tared 4 ounce aluminum dish, tinned ointment box, or glass dish. Dry to constant weight in an oven at 150°±2° C. Usually 45 minutes to 1 hour is sufficient. Soaps containing naphtha or as much as 1% glycerine give results too high on account of volatilization of these materials. Soaps containing silicate give results which are too low because some water is retained by the silicate. In these cases moisture should also be reported by difference after all other constituents have been determined.

Some soaps will char at 150° C. but may be dried satisfactorily at 105° C.; usually two hours are sufficient. Soaps from linseed and other oxidizing oils absorb oxygen and, if the oven is used, may gain in weight near the end of the test. For soaps from such oils or those containing naphtha and glycerine, the distillation method is much more satisfactory than any oven method.

Moisture (Distillation Method) [2, 3, 4]

For soaps containing from 5 to 25% of moisture and volatile matter use a 20 gm. (±0.04 gm.) sample. For soaps containing more than 25% moisture and volatile matter use a 10 gm. (±0.02 gm.) sample. The weighed sample is carefully transferred to a 500 ml. short-neck round bottom flask or an Erlenmeyer flask. Add approximately 10 gm. of anhydrous, fused sodium acetate to prevent violent frothing, and then follow with 100 ml. of xylene which has previously been saturated with water by shaking the xylene with a small quantity of water and distilling. Use the xylene distillate for the determination. Attach the flask to a graduated distilling tube receiver, such as the Bidwell-Sterling or Stark and Dean apparatus. The receiver should be calibrated at 25° C. and normally of 5 to 6 ml. capacity. It is connected to a reflux condenser (19″ Liebig). Prior to starting the determination, fill the receiver with saturated xylene by pouring in through the reflux condenser.

So that the refluxing will be under better control, wrap the flask and the tube leading to the receiver with asbestos cloth. Apply heat to the flask by means of a Argand gas burner or an electric heater and distill slowly. The rate at the start should be approximately 100 drops per minute. When the greater part of the water has apparently distilled over, increase the distillation rate to 200 drops per minute until no more water is collected. Purge the reflux condenser

[4] A. K. Church and J. H. Wilson, Soap, 7, 35, 1931.

during the distillation with 5 ml. portions of xylene to wash down any moisture adhering to the walls of the condenser. The water in the receiver may be made to separate from the xylene by using a spiral copper wire. Move the wire up and down in the condenser occasionally, this causing the water to settle to the bottom of the receiver. Reflux for at least two hours, after which the heat is turned off. Adjust the water distilled over into the receiver to 25° C. Read the volume of water and calculate the percentage of moisture in the soap, as follows:

$$\frac{\text{Volume in ml. at 25° C.} \times 0.997}{\text{Weight of sample}} \times 100 = \% \text{ moisture in soap.}$$

Total Fatty Acid, Fatty Anhydride, Combined Alkali, and Anhydrous Soap

(a) **Soaps Containing a Small Amount of, or No Coconut Oil.**—Weigh a 5±.01 gram sample on a tared watch glass, transfer to a 250 ml. beaker, and dissolve in 50 ml. of hot water. Transfer to a 250 ml. glass-stoppered extraction cylinder, make up to a volume of 100 ml., and cool. Add 3 drops of methyl orange and sufficient dilute H_2SO_4 (1 : 4) to give an excess of acid after decomposing the soap. Add 40 ml. of ethyl ether and shake gently until the contents are well mixed. Let the cylinder stand until the ether layer has separated clear. Draw off the ether layer into a tared 150 ml. Soxhlet flask through a slender glass siphon by means of suction. Wash the siphon by drawing a few ml. of ether through it. Repeat the extraction at least 3 more times, using 25 ml. of ether and shaking more vigorously after the first extraction. Silicated soaps and flakes which show a tendency to dry out should be extracted about 6 times. Combine all extracts in the same Soxhlet flask. If the extract is not clear transfer to another tared Soxhlet flask through a filter. Evaporate the ether from the Soxhlet flask by warming on the *edge of the steam bath.* Rapid evaporation will cause condensation of moisture in the flask. In case of soaps high (40% or higher) in coconut oil, evaporate only to about 50 ml. and proceed as in (*b*). For other soaps evaporate to dryness, and finally dry for 1 hour at 90°±2° C. Cool and reweigh. Dissolve the extracted fatty acids in about 40 ml. of hot, neutral alcohol, add a few drops of phenolphthalein indicator and titrate with N/1 NaOH to exact neutrality.

$$\frac{\text{Weight of fatty acids} \times 100}{\text{Weight of sample}} = \% \text{ total fatty acid.}$$

$$\frac{\text{NaOH titration} \times 0.9}{\text{Weight of sample}} = \% \text{ water equivalent to fatty acids.}$$

$$\% \text{ total fatty acid} - \% \text{ water equivalent} = \% \text{ "Fatty Anhydride."}$$

$$\frac{\text{NaOH titration} \times 3.1}{\text{Weight of sample}} = \% \text{ combined } Na_2O.$$

$$\frac{\text{NaOH titration} \times 4.7}{\text{Weight of sample}} = \% \text{ combined } K_2O.$$

$$\% \text{ fatty anhydride} + \% \text{ combined alkali} = \% \text{ "Real Soap" or Anhydrous Soap.}$$

(b) **Soaps High in Coconut Oil.**—If desired, this method may be used for any soap. It is often called the " soda soap " method.[2, 3]

Proceed with the extraction as for boiled soaps except that the extracts are collected in a 250 ml. beaker or Soxhlet flask. Partially evaporate the ether to not less than 50 ml. on the edge of a steam bath and add 50 ml. of hot, neutral alcohol redistilled over caustic. Add several drops of phenolphthalein indicator and titrate with N/1 NaOH to exact neutrality. Evaporate on the steam bath to dryness, and while the soap is in the form of a thick paste, swirl the beaker on its side, thus distributing the soap in a thin layer along the sides and bottom of the beaker.

Dry to constant weight in an oven at 105°±2° C. After a preliminary drying at 105° C. for an hour, drying may be continued at 150° C. On removal from the oven cool in a desiccator and weigh as soon as cool.

Correct for neutral salts in the caustic solution by determining the amount of salt per ml. by neutralizing 20 ml. of N/1 NaOH with N/1 HCl using phenolphthalein indicator and drying the residue to constant weight at 105° C. From the weight of the residue found, subtract the weight expected if the reagents had been 100% pure. The difference divided by 20 gives the correction per ml. for neutral salts. Subtract the product of the total fatty acid titration times the factor (0.022) plus correction for neutral salts from the weight of soda soap to obtain total fatty acids. Calculate as for boiled soap.

If the soap is a cold process soap containing superfat, i.e. unsaponified fat, and total fatty acids are required, it will be necessary to treat the sample after dissolving in water with 5 ml. (or more) of 50° Bé caustic potash solution. The solutions should be mixed thoroughly. With cover glass on the beaker, place over an opening in a steam bath, saponify for one hour with occasional stirring. Acidify with an excess of dilute H_2SO_4 (1 : 4) and proceed as above.

If the real soap in a soap containing superfat is desired, it will be necessary to determine the superfat including free fatty acid and unsaponifiable and to correct the total fatty acid as determined without further saponification.

Chlorides

Transfer the acid water in the cylinder from the total fatty acid extraction to a 250 ml. beaker, neutralize with chlorine-free N/1 NaOH and back titrate with N/1 H_2SO_4 to make the solution one drop on the acid side of neutral. Add 1 ml. of 10% potassium chromate indicator. Place over a Wratten Safelight—Filter No. 00 illuminated by a 200-watt Mazda light at distance of 12″. Titrate slowly with N/10 $AgNO_3$ solution, stirring vigorously. The addition of a little gum arabic may aid in the titration.

$$\frac{\text{Titration} \times 0.585}{\text{Weight of sample}} = \%\ \text{NaCl},$$

$$\frac{\text{Titration} \times 0.745}{\text{Weight of sample}} = \%\ \text{KCl}.$$

In case total anhydrous soap is not to be determined, it will be more convenient to use the following method. Dissolve 5±.01 grams of soap in 40 ml. of hot water, add 10 ml. 1 : 4 H_2SO_4 and heat on a steam bath or hot plate until

the fatty acids rise in a clear layer. Filter through a wet 9 cm. filter paper, collecting the filtrate in a 250 ml. beaker. Wash the fatty acids and filter paper with hot water until the total volume in the beaker is about 80 ml. Titrate as described above with N/1 NaOH and N/1 H_2SO_4 until the solution is one drop on the acid side of neutral. Titrate with N/10 $AgNO_3$ as described above.

A rapid method is that of Bennett.[2, 3, 5] Dissolve 5±.01 grams of the soap in 300 ml. of water, boiling if necessary to affect solution. Add an excess of chlorine-free magnesium nitrate solution (about 25 ml. of a 20% $Mg(NO_3)_2 \cdot 6H_2O$ solution). Without cooling or filtering, titrate with N/10 $AgNO_3$ as described above.

Unsaponified and Unsaponifiable Matter (A. C. S.[2]—A. O. C. S.[3])

The extraction cylinder used is a 250 ml. glass stoppered cylinder about 35 mm. in diameter and 300 mm. high. The solvent used is petroleum ether which should be of the pentane type, containing a minimum amount of iso-pentane, iso-hexane and hexane and conforms to the following specifications.[2, 3, 6]

*Distillation Test.**—

Initial boiling point—not less than 35° C. nor over 40° C.
Dry flask endpoint—not less than 50° C. nor over 60° C.
At least 95%, distilling under 55° C.
Not over 85% distilling under 40° C.

Specific gravity at 15.5° C.—0.630 to 0.675.
Color—water white. Doctor test—sweet.[7]
Evaporation residue—not over 0.002% by weight.
Copper strip corrosion test, A. S. T. M.—D130–30—Non-corrosive.
Unsaturated Compounds—trace only permitted.

Weigh a 5±.01 gram sample into a 250 ml. beaker. Add 100 ml. of 50% redistilled ethyl alcohol. Warm and stir to effect solution, keeping the temperature under 60° C. Filter off any undissolved residue on a Gooch crucible with an asbestos or paper pad into an extraction cylinder. Wash 3 times with hot 50% alcohol and then with 5 ml. of hot 95% alcohol. Complete the washing with a small amount of petroleum ether.

Make the volume of solution in the cylinder up to the 160 ml. mark with redistilled alcohol. Add 50 ml. of petroleum ether. Stopper with a rubber stopper which has been soaked in petroleum ether overnight to remove soluble matter. Shake vigorously for one minute and allow to settle until both layers are clear. The volume of the upper layer should be about 40 ml. Draw off the petroleum ether layer as closely as possible by means of a slender glass siphon into a 500 ml. pear-shaped separatory funnel containing 25 ml. of 10% alcohol containing a few drops of phenolphthalein. Take special care that none of the alcohol-soap layer is drawn off. Repeat the extraction at least 6 times, using

[5] H. C. Bennett, J. Ind. Eng. Chem., **13**, 813 (1921).

[6] Rules governing transactions between members of the National Cottonseed Products Association, 1937–38, page 133.

* Distillation test to be made according to A. S. T. M. method D86–27.

[7] R. C. Griffin, Technical Methods of Analysis, 2d edition, p. 235 (1927).

50 ml. of petroleum ether each time. Draw all the extracts into the same separatory funnel. When extraction is completed, stopper the separatory funnel vigorously for ½ minute to wash the extract. Draw off the alcohol layer and swirl the funnel to collect any drops of the washing solution at the bottom. Continue washing with two 5 ml. portions of 10% alcohol until the extract is free from alkali and soaps as shown by the absence of color in the alcohol layer. Transfer the washed extracts to a tared 150 ml. Soxhlet flask and rinse the separatory funnel several times with petroleum ether. Evaporate the solvent in a gentle current of dry air on the steam bath. Dry in an oven at 105° C. for 15 minutes. Cool and weigh. Dissolve the residue in 50 ml. of warm ethyl alcohol neutralized to phenolphthalein, titrate to the same color as the original neutral alcohol with N/25 sodium hydroxide solution and calculate to oleic acid. Deduct this figure from the gross weight of the residue previously found. Any blank residue from the petroleum ether must also be deducted from the weight of the residue. Report results as "Unsaponified and Unsaponifiable Matter."

Unsaponifiable Matter

Weigh 5±.01 gms. of the sample into a 200 ml. Erlenmeyer flask. Add 30 ml. of redistilled 95% ethyl alcohol and add 5 ml. of 50% aqueous KOH. Boil the mixture one hour under a reflux condenser. Transfer the solution to the extraction cylinder and wash the flask with 95% redistilled alcohol to the 40 ml. mark. Complete the transfer first with warm and then cold water until the total volume is 80 ml. Then wash the flask with a small quantity of petroleum ether. Cool the cylinder and contents to room temperature. Add 50 ml. of petroleum ether and proceed with the extraction as outlined under "Unsaponified and Unsaponifiable."

Weigh the residue and correct for fatty acids. Report the result as "Unsaponifiable Matter." Deduct the unsaponifiable result from that of the unsaponified and unsaponifiable and report the difference as "Unsaponified Matter."

For soaps containing lanolin, many more extractions for Unsaponified and Unsaponifiable will be required for complete removal. For any sample, thorough and vigorous shaking is necessary in order to bring the two phases into the most intimate contact possible.

Free Alkali or Free Fatty Acid

The methods outlined will not give absolutely accurate results for free alkali, but will give results sufficiently accurate for control or practical soap analyses. The accuracy is probably close to ±.01% Na_2O.

(a) **When "Builders" (or Fillers) Are Low in Amount and Are Not Determined.**—Weigh a 20 gm. sample (±.05) rapidly and transfer to a 500 ml. Erlenmeyer flask containing 100 ml. of hot, neutral 95% alcohol. Cover the flask with a watch glass and dissolve the soap as rapidly as possible by heating on the steam bath. Add a few drops of phenolphthalein and titrate rapidly with N/4 H_2SO_4 without filtering. Take the first endpoint, disregarding any subsequent return of color. Calculate to free Na_2O (or NaOH) or K_2O (or KOH) as the character of the soap indicates. If the alcoholic solution is acid to phenolphthalein, titrate with N/10 NaOH and calculate the percentage of

free fatty acid as oleic acid, or lauric acid if coconut soap. Save the solution for determination of carbonates.

(b) **When "Builders" Are Determined.**[3, 2]—Weigh a 10±.02 gm. sample and dissolve in 200 ml. of hot, neutral 95% alcohol. Filter through a 9 cm. filter paper into a 500 ml. Erlenmeyer flask and wash the residue three times with hot, neutral 95% alcohol. Protect from CO_2 and other acid fumes during filtration. If the soap contains borax, or phosphates, it can be washed with alcohol indefinitely without removing the apparent alkalinity. Cover the flask with a watch glass and heat to incipient boiling. Titrate with N/4 H_2SO_4 and report as "free Na_2O (or NaOH)" or "free K_2O (or KOH)" as the character of the soap indicates. If the alcohol is not pink, titrate with N/10 NaOH and report "free fatty acid" as oleic acid.

If potassium carbonate is present, the free KOH results will be high due to the solubility of K_2CO_3 in the alcohol. For liquid soaps containing free KOH and K_2CO_3 the following procedure has given satisfactory results: Weigh a 20 gm. sample of the soap solution into a 500 ml. Erlenmeyer flask. Add 10 gms. of neutral dry salt. Mix the salt with the soap thoroughly by shaking. Allow to stand 10 minutes covered by a watch glass. Add 20 ml. of hot neutral 95% alcohol. Shake thoroughly and place on the steam bath for 10 to 15 minutes, shaking occasionally. Filter through a neutral filter paper moistened with neutral alcohol into another 500 ml. Erlenmeyer flask. Retain most of the insoluble in the flask, if possible. Wash with 25 ml. of hot alcohol, pouring around the top of the paper so as to wash the paper at the same time. Give the paper a slight additional wash with neutral alcohol after the first has drained through. Allow to drain. Titrate with N/4 or N/2 acid, and from this calculate free K_2O.

Sodium Carbonate

(a) **If No "Builders" Are Present.**—Add from a burette 10 ml. of N/1 H_2SO_4 to the solution in the flask from the free alkalinity titration (*a*). Add 50 ml. of distilled water and boil gently for 1 hour, swirling the flask occasionally. Remove the flask, add 10 ml. N/1 NaOH and titrate with N/4 H_2SO_4 to the colorless endpoint. If this titration is more than 7.5 ml., add another 10 ml. portion of N/1 H_2SO_4 and again boil for 1 hour. Add 10 ml. N/1 NaOH and again titrate with N/4 H_2SO_4. Calculate the per cent carbonate from the acid titration.

(b) **If "Builders" Are Present.**—Dissolve the residue upon the filter paper from the free alkalinity determination (*b*) with hot water into the original beaker. If no insoluble matter other than insoluble SiO_2 from the builder is present, the filter paper should be punctured and the entire contents of the paper washed through. Continue washing until a few drops of phenolphthalein indicator dropped on the filter paper show only a very faint pink color. Cool the filtrate and titrate with N/1 H_2SO_4 using methyl orange indicator. Record the titration as the "carbonate titration" and in case no silicate is present, calculate direct to sodium carbonate. If silicate is present, it should be determined as indicated in the "Note" under "Determination of Silica Present as Alkaline Silicates." The above titration must then be corrected for the silica present in calculating the carbonate.

If potassium carbonate is present, it can best be determined from the CO_2 determination.

Determination of Carbon Dioxide (Gravimetric Method for Carbonates)

For most cases the volumetric methods described above are satisfactory, but when the highest accuracy is desired, a reliable absorption method should be used. The following method (A. C. S.—A. O. C. S.[2, 3]) has proved satisfactory.

A 250 ml. Erlenmeyer flask is placed on a gauze over a burner. The flask is equipped with a 2-hole rubber stopper, through one opening of which is a 10-inch reflux condenser and through the other a thistle tube equipped at the outer end with a 3-way stopcock. The lower end of the thistle tube is drawn to a small point, which is placed very close to the bottom of the flask. Then the straight-away end of the stopcock is attached to a small funnel for the introduction of acid to the flask. The other opening of the stopcock is attached to receive air from a purifying train consisting of a wash bottle containing concentrated sulfuric acid, and a second at the outer end of the train containing a 50% solution of potassium hydroxide. The top of the reflux condenser is attached first to a drying wash bottle containing concentrated sulfuric acid, and then to a weighed absorbing train consisting of a suitable potash bulb charged with 50% potassium hydroxide, and a second containing concentrated sulfuric acid. This train is attached to a protective U-tube containing calcium chloride. The U-tube is attached to an aspirator.

Procedure.—Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon dioxide-free air until the apparatus is freed of carbon dioxide. Insert the train and continue the aspiration for ½ hour. Check the weight of the train to determine if the air is passing through too fast, or if the system is free from carbon dioxide. The system must be free from leaks. Weigh out 1 or 2 gms. of the sample into the Erlenmeyer flask, cover with 20 ml. freshly boiled distilled water, close the apparatus with the train in place. Add 20 ml. dilute hydrochloric acid (1 : 1) through the funnel very slowly, with no heat being applied to the flask. The rate of adding acid should be carefully controlled so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to stop the gas flow, start heating gently and continue until the contents of the flask have boiled 15 to 20 minutes. Stop heating and continue aspirating until the flask has cooled down. Remove the train and weigh. Calculate increase of weight as carbon dioxide. Carbon dioxide multiplied by 2.41 equals sodium carbonate.

All connections should be made glass to glass. Apparatus with ground glass joints is available and is preferred. Ascarite-filled absorption bulbs and scrubbing tower instead of those using KOH are very satisfactory and convenient.

Determination of Silica Present as Alkaline Silicates [2, 3]

When the material contains no mineral matter that is insoluble in water,* ignite a sample of the soap containing not to exceed 0.2 gm. of silicate in a

* When water-insoluble mineral matter is present, take a portion of the solution after titration in (b), "Sodium Carbonate" equivalent to not more than 0.2 gm. silica, add 5 ml. concentrated HCl and proceed as above.

platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 ml. concentrated hydrochloric acid in excess. The dish or casserole containing the solution should be covered with a watch glass while adding acid so as to avoid loss by spray.

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on steam bath or hot plate at a temperature not exceeding 120° C. Cool, moisten with concentrated hydrochloric acid, let stand 5 to 10 minutes, breaking up all lumps with a stirring rod. Add about 25 ml. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper*

Carefully dry the filter papers and residue at 150° C. in a tared platinum crucible, ignite at as low a temperature [8] as possible until the paper is consumed, then raise the temperature and heat to constant weight in a muffle or over a blast lamp. Cool in a desiccator and reweigh. If extreme accuracy is desired, moisten the residue in the crucible with water, add 5 ml. hydrofluoric acid and 4 drops of concentrated sulfuric acid, evaporate to dryness, and ignite as before for about 2 minutes. Cool in a desiccator and reweigh. The difference between this weight and the previous weight is the weight of SiO_2.[9]

To calculate sodium silicate (1 Na_2O : 3.25 SiO_2) multiply SiO_2 by 1.308.[10]

NOTE.—In case carbonates have been determined as under (*b*), the filtrate may be used for the silicate determination. In that case, add 5 ml. of concentrated hydrochloric acid to the solution in the beaker, evaporate to dryness and proceed as above.

Borax

Qualitative Test.—A qualitative test may be made by wetting a piece of turmeric test paper with a few ml. of the SiO_2 filtrate. If the paper on drying in air turns a brick red, a borate or perborate is present. To determine if the coloration is due to perborate, dissolve about 2 grams of the original sample in about 100 ml. of a 5% potassium iodide solution containing 2 ml. of starch solution. Add 10 ml. of 1 : 4 sulfuric acid and stir. A blue solution denotes the presence of an oxidizing agent which with a positive turmeric test can be assumed as indicating the presence of perborate.

Quantitative Test.—To determine borate quantitatively in case silicates are not present, weigh 10±.02 grams of the soap (5±.01 grams if more than 5% borax is present), transfer to a 250 ml. beaker and break up the soap with 50 ml. of water and 50 ml. of N/1 H_2SO_4. If the solution is not distinctly red to methyl orange, add N/1 H_2SO_4 until it is acid. Do not heat longer than

* The filtrate may be collected in a 250 ml. volumetric flask and used for qualitative and quantitative phosphate.

[8] K. A. Krieger and H. S. Lukens, Ind. Eng. Chem., Anal. Ed., **8**, 118 (1936).

[9] W. F. Hillebrand, The Analysis of Silicate and Carbonate Rocks, U. S. Geological Survey, Bulletin 700, 102.

[10] Report of the Soap Analysis Committee, A. O. C. S., Oil and Soap, **12**, 10 (1935).

necessary. Filter off the fatty acids through a wet paper, wash well with hot water, adding all washings to the filtrate. Neutralize to methyl orange with N/1 NaOH and note the reading. Add a few drops of phenolphthalein and titrate to the endpoint with N/1 NaOH.

Add about 1 gram of neutral mannitol and again titrate very slowly. Add 1 gram more of the mannitol and titrate again and repeat this process until mannitol causes no further action on the endpoint. If phosphate and borate are both present and no silicate, add 1 gm. of sodium chloride with the mannitol before titrating. Calculate the number of milliliters of sodium hydroxide added from the methyl orange endpoint to the final endpoint of % $Na_2B_4O_7$ by multiplying by 0.503 or to % $Na_2B_4O_7 \cdot 10H_2O$ multiplying by 0.954 for 10 gm. samples. In case phosphate is present, a correction must be made since part of the phosphate is titrated in the borate titration. For a 10 gm. sample the following formula is used:

$$[\text{"Borate Titration"} - (\%\ Na_3PO_4 \times 0.61)] \times 0.503 = \%\ Na_2B_4O_7$$

Since silicic acid affects the phenolphthalein and methyl orange endpoints in the mannitol titration, it must be removed by the following method. Weigh a 5 gm. sample in a tared platinum dish and ignite over a low flame until all of the organic matter has been burned off, *but do not ash the salts.* Cool the dish and contents and place it in a beaker. Add about 100 ml. of water and boil until the residue is removed from the dish. Wash the contents of the beaker into a 500 ml. distillation flask, add 15 ml. of concentrated hydrochloric acid, and distill to dryness. Pour the distillate back into the distillation flask and repeat. Cool and wash the contents of the flask into the beaker containing the distillate. Filter through a quantitative filter paper and wash well. Stir the filtrate with a stick of caustic until not quite neutral to methyl orange. Neutralize with N/1 NaOH and continue titration as above with mannitol. Correct calculations for phosphate in the same manner as above.

Perborates

Weigh a 1 gm. sample and transfer to a 300 ml. Erlenmeyer flask with cold water. Make up to about 80 ml. Acidify immediately with 20 ml. of N/1 sulfuric acid and titrate at once with N/10 potassium permanganate. One ml. of potassium permanganate is equivalent to 0.0008 gms. of oxygen, 0.007694 gms. of $NaBO_3 \cdot 4H_2O$, and 0.00409 gms. of $NaBO_3$.

Phosphates

A Qualitative Test for Phosphate May Be Made on the Filtrate from the SiO_2 Determination.—If meta- or pyrophosphates are present add about 10 ml. of nitric acid and hold at near boiling temperature over night to convert them to orthophosphates. To 20 ml. add 2 ml. of concentrated nitric acid and 5 ml. of 30% NH_4NO_3 solution, phosphate-free. Heat to boiling and add 20 ml. of ammonium molybdate solution. Let the solution stand 20 minutes on the steam bath. If a yellow precipitate forms, a phosphate is present.

Quantitative Determination [2, 3]—Pipette an aliquot corresponding to 0.50 gm. or 1 gm. into a 250 ml. beaker; add ammonium hydroxide in slight excess;

and barely dissolve the precipitate formed with a few drops of nitric acid, stirring vigorously. Add about 15 gms. of dry ammonium nitrate or a solution containing that amount.

To the hot solution add 70 ml. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) present. Digest at about 65° C. for an hour, and determine if the phosphoric acid has been completely precipitated by the addition of more molybdate solution to the clear supernatant liquid. Filter, and wash with cold water or, preferably, 10% ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide (1 : 1) and hot water, and wash into a beaker to a bulk of not more than 100 ml. Neutralize with hydrochloric acid, using litmus paper or bromthymol blue as an indicator, cool, and from a burette add slowly (about 1 drop per second), stirring vigorously, 15 ml. of magnesia mixture * for each decigram of phosphoric acid (P_2O_5) present. After 15 minutes add 12 ml. of ammonium hydroxide (sp.gr. 0.90). Let stand till the supernatant liquid is clear (2 hrs. is usually enough) filter, wash the precipitate with dilute ammonium hydroxide (1 : 10) until the washings are practically free from chlorides; dry, burn first at a low heat and ignite to constant weight, preferably in an electric furnace, at 950°–1000° C.; cool in a desiccator, and weigh as $Mg_2P_2O_7$. Calculate and report the result as percentage of P_2O_5 or alkaline phosphate known to be present.

Sulfates

Weigh a 50 gm. sample, dissolve in water, break up the soap with 35 ml. of concentrated hydrochloric acid and filter off insoluble matter and fatty acids through a wet filter paper. Wash the filter well with cold water. If silicate is present, remove it by evaporation and filtration as in the silicate determination. In either case make up the silicate-free filtrate to 175 ml. with water, add 5 ml. of hydrochloric acid and boil. To the boiling solution, add 15 ml. to 20 ml. of a 10% barium chloride solution, drop by drop. Continue boiling until the precipitate is well formed and keep at a temperature of about 70° C. for one hour or until the precipitate settles well. Filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate. Calculate to sodium sulfate or to sulfate known to be present.

Total Alcohol Insoluble Matter [2, 3]

Digest hot a 2 to 10 gm. (±0.01 gm.) sample with 200 ml. of freshly boiled ethyl alcohol neutral to phenolphthalein (94% or higher). Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap. Dry the filter paper, or crucible, and residue at 100° to 105° C. for 3 hours, cool, and weigh the total matter insoluble in alcohol. (The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates and sulfates, as well as starch, and may be used for the approximate determination of these

* Magnesia mixture—Dissolve 55 gms. of crystallized magnesium chloride ($MgCl_2 \cdot 6H_2O$) in water, add 140 gms. of ammonium chloride, 130.5 ml. of ammonium hydroxide (sp.gr. 0.90), and dilute to 1 liter.

constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used.)

Water Insoluble Matter [2, 3]

Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, extract it with water at 60° C. and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100° to 105° C. for 3 hrs., cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

Glycerine, Starch, and Sugar

The sample sizes indicated are for ordinary soap. If soaps high in glycerine or sugar are analyzed, sample sizes should be reduced and the amount of bichromate and acid increased. Transparent soaps are frequently high in glycerine and sugar.

1. Glycerine when starch and sugar are not present: Weigh a 25 gm. sample, transfer to a 400 ml. beaker and dissolve the soap in about 100 ml. of water. Add about 25 ml. 1 : 4 sulfuric acid and break up the soap. Do not heat longer than necessary. Filter off the fatty acids, collecting the filtrate in a 250 ml. volumetric flask. Make up to volume * and pipette 50 ml. into a 250 ml. Erlenmeyer flask containing 0.7456 gm. of dry potassium bichromate of highest purity (equivalent to 0.1 gm. of glycerin), 10 ml. of water, and 15 ml. concentrated sulfuric acid. Cover the flask with a watch glass and heat in a steam bath for 2 hours at a temperature of 93° to 100° C.† Cool, and titrate with standardized ferrous ammonium sulfate (about 300 gms. per liter), using potassium ferricyanide as an outside indicator, or by use of an electrometric titration apparatus. The ferrous ammonium sulfate solution must be of such strength that 0.7456 gm. of potassium bichromate will be required for complete oxidation of the iron in 19.5—20.0 ml. of the solution. It should contain 100 ml. of sulfuric acid per liter of solution. A blank test must be run exactly the same with omission of the sample.

$$\frac{2\ (\text{Blank titration} - \text{Sample titration})}{\text{Blank titration}} = \text{per cent glycerine.}$$

Note.—The electrometric titration apparatus (Ind. Eng. Chem., Anal. Ed. 9, 514 (1937)) is more rapid and in the hands of the average analyst more accurate than the outside indicator with the spot plate. The preferred set-up is one using platinum and tungsten electrodes. By a suitable resistance the galvanometer is adjusted to zero. At the endpoint the needle is deflected to the end of the scale. A glass stirrer directly connected to a suitable motor is used. By use of a wide-mouthed Erlenmeyer for oxidation flask, there is ample room for the electrodes, stirrer, and burette tip which is, usually, extended and bent to allow the burette to be several inches to one side of the motor. A calomel half-cell may be used instead of the tungsten electrode with the use of N/1 KCl solution.

* If appreciable amounts of salt or soluble fatty acids are present, they may be precipitated by addition of 0.25 gm. of silver sulfate at this point. Shake well, let settle and filter a 50 ml. portion for analysis.

† If the solution turns blue during oxidation, or if the back titration is less than 4 ml., 1.4912 gms. of potassium bichromate must be used or a smaller sample taken.

2. Glycerin in presence of starch but no sugar:[2, 3, 11] Weigh a 25 gm. sample, dissolve in 100 ml. of *warm* water (not above 70° C.), filter off the water-insoluble matter, and wash the residue twice with warm water (not above 70° C.). Add 25 ml. of 1 : 4 sulfuric acid to the filtrate to break up the soap. Filter off the fatty acids and wash thoroughly, catching the filtrate in a 250 ml. volumetric flask. Determine the amount of glycerine by the method above. Make to volume and pipette 50 ml. into the Erlenmeyer.

3. Determination of sugar (Munson and Walker Method):‡ Proceed as for glycerin above, filtering off any starch or insoluble matter, but using hydrochloric acid (1 : 1) to break up the soap and boiling to invert the sugars. Transfer to a 250 ml. volumetric flask, neutralize to litmus with NaOH, and make to volume. Transfer 25 ml. each of copper sulfate and alkaline tartrate Fehling's solutions to a 400 ml. beaker and add an accurately measured 50 ml. aliquot of the invert sugar solution. Heat so that boiling begins in four minutes, and continue boiling for exactly two minutes. Keep the beaker covered during boiling. Filter the cuprous oxide at once in a prepared Gooch crucible and wash thoroughly with hot water (about 60° C.), and finally with 10 ml. of alcohol and 10 ml. of ether. Dry for 30 minutes at 105° C., cool and reweigh. Refer to Table 9, Chapter XLII, Methods of Analysis, A. O. A. C. (1935) to determine the amount of invert sugar equivalent to the weight of cuprous oxide. The weight of invert sugar multiplied by 0.95 equals the weight of sucrose.

4. Determination of glycerine in presence of sugar:[11] If starch is present, it must be filtered off as directed in (2); then proceed as directed in (1), except boil the solution when acid 20–30 minutes to secure complete inversion and to remove alcohol, increase the bichromate to 2 to 3 times the amount specified and the H_2SO_4 to 25 ml. Determine the weight of invert sugar as directed in (3). The oxidation of sugar is taken care of by calculating the glycerin by the following formula for 25 gm. sample made to 250 ml. and 50 ml. aliquot.

$$\frac{2n\ (\text{Blank titration} - \text{Sample titration})}{\text{Blank titration}} - 17.51\ W = \text{per cent glycerine}$$

when W is the weight of *invert* sugar in an aliquot equal to a 5 gm. sample, and n is equal to number of times 0.7456 gms. of bichromate is used.

5. Determination of starch (A. C. S.—A. O. C. S.):[2, 3] Separate the water-insoluble matter as directed in (2) using a weight of sample that will give less than 3 gms. of starch. Transfer the insoluble matter, without drying, to a 500 ml. Erlenmeyer flask with hot water. Make up to 150 ml. and add 20 ml. of concentrated hydrochloric acid. Boil for 2½ hours under a reflux condenser, nearly neutralize with sodium hydroxide, and cool. Transfer to a 250 ml. volumetric flask, make up to volume and determine reducing sugars as directed in (3). Refer to the amount of dextrose equivalent to the weight of cuprous oxide. This weight multiplied by 0.90 equals the weight of starch.

[11] L. F. Hoyt and H. V. Pemberton, J. Ind. Eng. Chem. **14**, 54 (1922); correction, **14**, 340 (1922).

‡ L. S. Munson and P. H. Walker, J. Am. Chem. Soc., **28**, 663 (1906). P. H. Walker, **29**, 541 (1907). Official and Tentative Methods of Analysis of the A. O. A. C., 1935, 479, 626.

Volatile Hydrocarbons [2, 12, 13]

This method requires a source of dry, oil-free steam which is passed through the sample treated with acid, sufficient to liberate the fatty acids from the soap. The steam is next passed through strong caustic solution to scrub out any volatile fatty acids while the volatile hydrocarbons are condensed with the steam in a suitable arrangement which allows the excess water to flow away, leaving the volatile hydrocarbon in the measuring burette. The method may be applied to samples containing substances immiscible with water and volatile with steam. For solvents heavier than water a Bidwell-Sterling tube should be used.

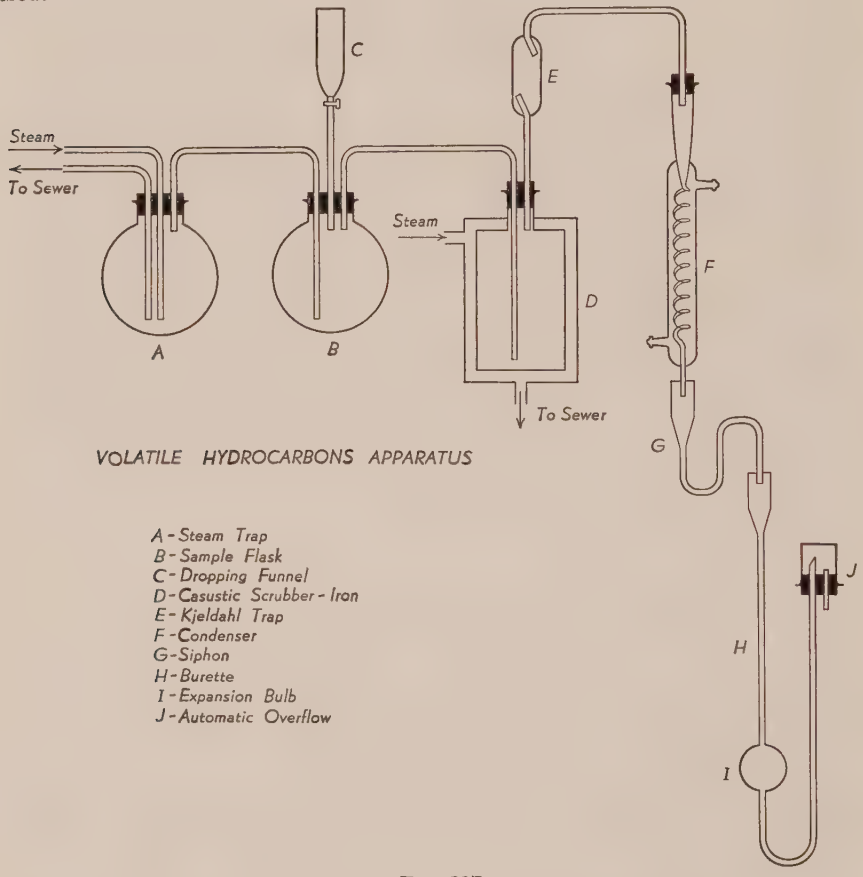


Fig. 287

Apparatus.—The apparatus and its arrangement are shown in the sketch. The following are the important items, lettered to correspond to the lettering of the sketch (Fig. 287).

[12] Determination of Volatile Hydrocarbons in Soaps, Oil and Soap, **13**, 9 (1936).
[13] Report of Soap Analysis Committee A. O. C. S., 1935, Oil and Soap, **13**, 7 (1936).

Steam Trap, *A*, a liter round-bottom ring-neck flask equipped with a siphon tube to the drain from the bottom of the flask and provided with a means of regulating the steam flow into the flask.

Evolution or sample flask, *B*, a liter round-bottom ring-neck flask. In case large samples are desirable the size of this flask may be increased.

Caustic scrubber flask, *D*, a steam jacketed metal flask is preferred, but a liter Florence flask provided with a steam coil of $\frac{1}{8}''$ copper tubing around the upper half may be used. If the glass flask is used it should be provided with a safety bucket below it and should be renewed frequently since the strong caustic dissolves the glass rather rapidly. This flask should be connected to the condenser by a Kjeldahl connecting tube, *E*, or similar safety device.

The inlet tubes for the steam into the evolution and scrubber flasks should extend nearly to the bottom of the flasks and be bent at right angles and parallel to the sides of the flask.

Condenser, *F*, a 12″ or longer spiral condenser of sufficient bore so the condensate will not readily close it.

Measuring burette, *H*, a 10 ml. burette calibrated to 0.1 ml. and carrying a bulb, *I*, approximately 100 ml. capacity, at the lower end.

The stoppers used should be of a good grade of rubber and should have been thoroughly cleaned free from any surface sulfur and should be given a steam distillation in position for several hours before use on a sample.

Insulating the flasks and tubing to reduce condensation aids distillation and its control.

Determination.—Place 150 ml. NaOH solution (about 46° Bé) and several sticks of solid NaOH, to provide against dilution, in the scrubber flask. Rinse out the condenser and burette with acetone. Attach a rubber tubing to the lower end of the burette, fill the burette and tubing with water and raise the outer end of the tubing so that the water level in the burette is near the top of the scale when the water is flowing to the drain from the automatic overflow, *J*. Be sure the connections are tight and that the tubing contains no air bubbles. Place the condenser in position so the lower end extends directly into the upper end of the burette just above the water level or connect to an adapter siphon, *G*, which discharges into the burette. The cooling water should be 15.5° C. or colder. Ice water may be desirable for low boiling hydrocarbons.

Weigh 100 ± 0.5 gms. of the soap (cut into cubes of about 1 cm. edges) or 50 ± 0.3 gms. of soap powder and transfer to the evolution flask. Add about 10 gms. of gum arabic (commercial) and 100 ml. of distilled water. Place the flask in position with 100 ml. of 1 : 3 H_2SO_4 in a dropping funnel, *C*, carried in the stopper. Connect the steam evolution, and wash flasks and condenser into position, making sure that the stoppers are tight-fitting and held in place by wiring. Rubber connections in the lines between the evolution flask and condenser should be avoided.

Add the acid to the sample slowly to avoid excessive frothing. While adding the acid, turn on the steam cautiously so adjusting the pressure by a bleeder valve that just enough steam flows to prevent any liquid backing into the steam trap flask.

When all the acid has been added, turn on enough steam to cause brisk distillation, taking care that no liquid is carried over from the evolution and wash flasks and that the condenser water does not become warm.

Continue the distillation until there is no increase in the volume of the upper layer for 45 minutes or no small droplets can be noted in the condensate.

When distillation is completed, shut off and drain condenser water and allow the steam to heat up the condenser to drive out the last traces of volatile hydrocarbon. Shut off the steam as soon as vapor begins to issue from the lower end of the condenser. Immediately open the stopcock of the dropping funnel to prevent caustic being drawn into the evolution flask.

Stopper the burette and allow its contents to come to room temperature or bring them to a definite temperature by placing the burette in a water bath held at 25° C. for one to two hours.

Read the volume of the upper layer to the nearest .01 ml. The volume times the specific gravity equals the weight of the volatile hydrocarbon. The specific gravity should be determined at the temperature at which the volume is read. A small Sprengel tube made of 3 mm. glass tubing is convenient for this purpose.

Calculation.—

$$\frac{\text{ml. of volatile hydrocarbon} \times \text{specific gravity} \times 100}{\text{Weight of sample}} = \text{per cent volatile hydrocarbon.}$$

For some samples the volatile hydrocarbon content may be so low that a larger sample than 50 or 100 gms. is desirable. The size of the evolution flask may need to be increased if larger samples are used. The amount of water in the evolution flask and acid used should also be correspondingly increased.

Titer Test

1. Preparation of Total Fatty Matter (Fatty and Rosin Acids and Unsaponifiable Matter.—Dissolve 200 gms. of soap * in 200 ml. of water in a liter Erlenmeyer flask, add 20 ml. of 1 : 3 sulfuric acid and heat until the fatty matter collects in a clear layer.

The flask should be covered with a watch glass. Much time is saved by placing the sample in a liter beaker and using a motor-driven stirrer to keep constant agitation. Siphon off the acid water layer and decant the fatty matter through a dry filter paper into tall form, lipless 180 ml. beaker. If droplets of water can be seen, refilter the fatty acids through a dry filter paper.

2. Determination.—A standard titer thermometer [14, 15] graduated at zero and in tenths degrees from 10° to 65° C. is used or in .20 from—2° C. to 66° C. It should be certified by the United States Bureau of Standards, or carefully standardized against a certified thermometer. Special thermometers (graduated in tenths degree Centigrade) in 20° C. ranges from 0°–80° C. may be used.

After the fatty acids are dry, cool carefully by immersing in and out of water at about 17° C. until a cloud begins to form, stirring continuously with the thermometer (about 150 r.p.m.) so that no crust forms on the sides or bottom

* The fatty matter obtained is also used for the iodine value, saponification value, and may be used for rosin determinations. If the soap contains superfat, it must be saponified with glycerol-potash as in the titer determination for fats.[15]

[14] Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 4th edition, 1935, 408.

[15] J. Ind. Eng. Chem., **18**, 1349 (1926).

of the beaker. Care must be taken not to cool too rapidly or low results will be obtained. Hold the beaker in the air and continue stirring more slowly (about 100 r.p.m.) until the mercury remains stationary for 30 seconds or begins to rise within that time. Wipe the outside of the beaker dry and carefully place the beaker and contents in a suitable container (air-jacket) submerged in water, or in ice, salt, water mixtures when necessary, maintained at a temperature of 10° C. below the titer. For titers above 30° C. the temperature should be 20° C. Allow the thermometer to hang without any disturbance with the bulb in the center of the fatty acids and follow the thermometer readings. Record the highest point to which the mercury rises as the titer of the fatty acids.

When not enough soap or fatty matter is available, the official method of the A. C. S.[15]—A. O. C. S.[3] should be used. This method, which differs slightly in details and requires less fatty acids, may also be used on the fatty acids obtained in the above procedure.

Iodine Value [15]

The iodine value is determined on the fatty matter obtained in the above procedure for titer test by the Wijs' method. If rosin is present this method cannot be used.* The solutions required are Wijs' iodine monochloride solution,[16, 15] standard N/10 sodium thiosulfate, 5% potassium iodide solution, U. S. P. chloroform, and starch indicator. Weigh exactly a sample of such size that at least 100% to 150% of the amount of iodine absorbed remains in excess, on a watch glass and transfer to a clean, dry 500 ml. glass-stoppered bottle, washing the watch glass thoroughly with 20–30 ml. of chloroform. Add 25 ml. of iodine monochloride and at the same time prepare a blank with the same amount of chloroform and iodine monochloride. Mix the contents gently and immediately put the bottles in a dark place at a temperature of 75°–90° F. for exactly 30 minutes. Add 20 ml. of 5% potassium iodide to the sample and blank followed at once by 100 ml. of water. Titrate with N/10 sodium thiosulfate, using starch solution as an indicator. Do not add starch until the solution has a pale straw yellow color. Toward the end of the reaction stopper the bottle and shake violently. The number of cubic centimeters of standard thiosulfate solution used for the blank minus the amount used for the sample, gives the thiosulfate equivalent of the iodine absorbed by the amount of sample used in the determination. Calculate to per cent iodine absorbed. Mechanical agitation using a small variable-speed motor attached to a glass stirrer is an advantage. It is necessary to use a wide mouthed glass-stoppered bottle.

Saponification Value

Weigh exactly a 5 gm. sample of the fatty matter obtained in the titer determination and wash into a 300 ml. Erlenmeyer flask with hot, neutral, redistilled

* In case the iodine value must be obtained on samples containing rosin, a 0.1 gm. sample is dissolved in 20 ml. of glacial acetic acid and 20 ml. chloroform in the glass-stoppered bottle. Immerse the bottle in water at a temperature of 21.5°–22.5° C. for 30 minutes. Add the Wijs' solution as above and maintain the temperature at 21.5°–22.5° C. for one hour. Other operations are the same as above.

[16] P. C. McIlhiney, J. Am. Chem. Soc., **29**, 1222 (1907).

95% alcohol and add 50 ml. of an approximately 0.7/N alcoholic-potash solution. Prepare a blank in the same manner, omitting the sample. Insert a funnel in the neck of the flask and saponify for exactly one hour, swirling the contents occasionally. Cool quickly and titrate at once with N/2 hydrochloric acid, using phenolphthalein indicator. Calculate the milligrams of potassium hydroxide required to saponify one gm. of fat by multiplying the difference between the blank and sample titrations by 5.61 and report as saponification value.

Acid Value

Weigh a 2 gm. sample of the fatty matter obtained in the titer determination and transfer to a 300 ml. Erlenmeyer flask with 50 ml. of hot, neutral 95% alcohol. Titrate with N/1 alkali, using phenolphthalein indicator. Calculate the milligrams of potassium hydroxide per gm. of fat by multiplying the ml. of N/1 alkali used by 28 and report as acid value.

Rosin in Fatty Acids [17] (A. C. S.[2]—A. O. C. S.[10]

Wolff's Method, Modified—Preparation of Fatty and Rosin Acids.—Dissolve 5 gm.±0.01 gm. of the sample in 100 to 200 ml. of hot distilled water in a 250 ml. beaker, add a slight excess of dilute sulfuric acid (1 : 1), heat on the steam bath until the fatty acids collect in a clear layer, cool to room temperature, transfer to a separatory funnel, washing the beaker free from fatty and rosin acids with small portions of ethyl ether, adding the ether washings to the separatory funnel. Add about 50 ml. of ethyl ether to the separatory funnel which is then given a whirling movement to dissolve the fatty and rosin acids. After the solid acids are dissolved in the ether, allow the aqueous solution to stand for at least five minutes. Draw off the aqueous portion into another separatory funnel designated as No. 2, add about 30 ml. of ethyl ether to funnel No. 2, shake vigorously, allow to stand for at least five minutes and then draw off the aqueous portion into another separatory funnel designated as No. 3. Transfer the ether extract to separatory funnel No. 1. Wash the aqueous liquid three more times, using for each washing about 30 ml. of ethyl ether. Then discard the aqueous liquid and add the ether washings to funnel No. 1. Now add about 50 ml. of distilled water to the collective ether extract in funnel designated as No. 1, shake vigorously and allow to stand for five minutes. Draw off the aqueous solution into another separatory funnel. Repeat this operation, combining the water washings until the ether is free from acid, using methyl orange as indicator. Add 50 ml. of ethyl ether to the water washings, shake the separatory funnel vigorously and allow to stand for at least five minutes. Draw off and discard the aqueous solution and wash the ether layer with small portions of distilled water until free from acid, using methyl orange as indicator. Transfer the total ether extract to a 250 ml. Erlenmeyer flask, evaporate off the ether slowly on a steam bath and dry one hour in an oven at 105° C., cool and dissolve in 20 ml. of absolute alcohol.

First Esterification.—Add 10 ml. of a solution of one volume of concentrated sulfuric acid (sp.gr. 1.84) and four volumes of absolute ethyl alcohol, bring to

[17] Chemical Ztg., **38**, 369, 382, 430 (1914); C. A., **8**, 2495 (1914).

boil on the steam bath and boil exactly four minutes under a reflux condenser. Remove from the steam bath, add to the liquid about five times its volume of 7 to 10% sodium chloride solution. Transfer to a separatory funnel, washing the Erlenmeyer flask with small portions of ethyl ether, the ether washing being added to the aqueous solution in the separatory funnel. Add about 30 ml. of ethyl ether to the separatory funnel, shake vigorously, and allow to stand for at least five minutes. Draw off the aqueous solution into another separatory funnel designated as No. 2. Add about 30 ml. of ether to funnel No. 2, shake vigorously, allow to stand for at least five minutes and then draw off the aqueous layer into another separatory funnel designated as No. 3. Repeat the extraction of the aqueous solution three more times. Then discard the aqueous liquid and add the combined ether solutions to separatory funnel No. 1. Add 50 ml. of sodium chloride solution (7–10%) to the ether extract in funnel No. 1, shake vigorously and allow to stand for at least 5 minutes.

Draw off the aqueous solution into another separatory funnel. Repeat this operation until the washings are neutral to methyl orange, all salt water washings being combined. Add 50 ml. of ether to the washings in the separatory funnel. Shake the funnel vigorously, allow to stand for at least five minutes and then draw off and discard the aqueous salt solution. Add 50 ml. of sodium chloride solution and wash the ether layer until the aqueous salt solution is neutral to methyl orange. Dry the ether extract by the addition of about 3 gm. of anhydrous sodium sulfate to the separatory funnel, filter into a 250 ml. Erlenmeyer flask and evaporate off the ether slowly on the steam bath to dryness.

Second Esterification.—Cool and dissolve the residue in 20 ml. of absolute ethyl alcohol and then proceed as above under "First Esterification." Add 30 ml. of neutral alcohol (94% or higher) and titrate rosin or rosin soap as desired, using phenolphthalein as indicator. (1 ml. N/2 alkali = 0.173 gm. rosin or 0.188 gm. rosin soda soap.) If the true fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap (real soap) obtained under total fatty acid determination.

The above method gives somewhat high results on all low percentages of rosin. On the higher percentages, it is approximately correct. In all cases where the rosin content is found to be less than 5%, the actual presence or absence of rosin should be checked qualitatively by the Lieberman-Storch test, which is as follows:

One to 2 ml. of the sample of fatty acids are shaken in a test tube with 5 to 10 ml. acetic anhydride, reagent grade, with gentle warming on a steam bath. After cooling, pour 1 to 2 ml. in a white porcelain dish and allow a drop or two of sulfuric acid (sp.gr. 1.53) to run down the side of the vessel. If rosin is present, a fugitive violet coloration changing to a brownish tinge is immediately produced at the margin of contact of the reagents. The test should be checked with a sample of fatty acids to which a small amount of rosin has been added.

(Sulfuric acid of 1.53 sp.gr. is prepared by diluting 34.7 ml. of concentrated sulfuric acid (sp.gr. 1.84), reagent grade, with 35.7 ml. of distilled water.)

WATER ANALYSIS

Probably at no other time has the importance of a water supply, either for domestic or industrial purposes, been so great, as in these early years of the twentieth century. The increasing realization of the effect of contaminating materials, both organic and inorganic, on a municipal or private drinking supply —and history's record of the devastating nature of epidemics due to water-borne disease organisms, have led to the careful investigation of water for its sanitary value and the development of materials and equipment to fight and eliminate such contamination, and have increased many hundreds of per cent the factor of safety to the public health. In like manner, and even to a greater extent, has the value of water for industrial uses been a matter for careful consideration. It is hard for the public to realize the immense quantities of water used for industrial purposes, not only for the development of steam and electric power, but also for purposes of manufacture.

From the standpoint of power development we are familiar with the heat losses and the increased operating expenses due to scale formation in the steam or locomotive boiler, and also to the continued rapid decrease in value of boiler property, or of power plant property, due to corrosion or rusting. Another element of trouble which is noticed not so much in stationary boiler practice as in locomotive boiler practice, is the element of foaming and priming of a water, which results in much more rapidly putting the steam raiser out of active service than either of the other types of trouble.

From the standpoint of plant deterioration due to rusting and corrosion one has only to look to the great mass of works on the corrosion of iron and steel which are largely results of the growing need for some information as to the cause and possible prevention of this particular phase of trouble.

In the world of industry the action of a hard water upon soap consumption has been known for centuries, and for a considerable period of time the value of a water was determined largely by the amount of soap that it would consume and render insoluble. This same hardness has a noticeable effect in the textile industry, in bleaching and dyeing, in the canning industry, especially when the water supply contains such substances in large quantities. In the photographic industry the presence of chlorides in water and certain alkalies is a source of considerable trouble, and in every case, before any intelligent effort can be made to overcome these troubles, a complete analysis of the water is necessary.

It shall be our purpose in the methods which follow to give, where it is possible, first a system of analysis whereby a complete analysis can be made, and to follow this up with optional methods which, individually, are equally as good as those occurring in the system of analysis, and in some cases more satisfactory where the laboratory has the required equipment, adding any special methods which may be found available.

Chapter by D. K. French.

SANITARY ANALYSIS

A sanitary analysis consists in the physical examination covering turbidity, color, odor and occasionally taste, the chemical analysis for total residue, loss on ignition and fixed solids, noting, where possible, the odor during ignition and also noting the appearance as regards color of the residue both before and after ignition, the determination of free and albuminoid ammonia, nitrogen as nitrite and nitrate, chlorine as chloride and oxygen consumed. Organic nitrogen is frequently determined upon polluted waters.

In sanitary analysis the principal determinations relate to the various forms and compounds in which nitrogen appears.

Organic Nitrogen.—The initial form can be determined as such, or as is usually the case in all but highly polluted supplies, as albuminoid ammonia which gives a very close approximate. By decomposition the organic matter first gives nitrogen as free ammonia, then, by oxidation, nitrogen as nitrites, and finally the more stable form of nitrogen as nitrates is reached. Conversely the reactions are frequently reversed through the influence of bacteria and microscopic organisms.

Chlorine is determined and by its excess over the normal chlorine of a general district may indicate previous sewage contamination.

Oxygen Consumed, or " oxygen required," means the amount which carbonaceous organic compounds present consume in the presence of potassium permanganate and acid. From these figures additional evidence is obtained as to the sanitary character of a water, though many phases of interference can occur.

PHYSICAL TESTS

For the physical examination, standards for turbidity and color have been adopted.

Turbidity.—Turbidity standards are based on parts per million of silica (SiO_2) suspended in water, and the adopted standard is that of the United States Geological Survey (A. P. H. A., p. 7). A water with a turbidity of 100 is one which has 100 p.p.m. of silica (SiO_2) in such a state of fineness that a bright platinum wire 1 mm. in diameter can just be seen when center of said wire is 100 mm. below the surface of the water and the observer is 1.2 meters above the wire. The observation must be in open air, not in sunlight, and in the middle of the day. Standards are prepared with precipitated fuller's earth (to pass 200-mesh sieve). One gram to one liter of distilled water makes a stock solution with 1000 turbidity. Standards for comparison are obtained by dilution.

The Illinois Water Supply Association outlines another method (Proc. I. W. S. A., 1914, pp. 49–51), whereby a suspension is prepared by shaking silica

(SiO_2) or fuller's earth (ground to pass a 200-mesh sieve), settling for ten hours, and determining by evaporating and weighing the amount of silica (SiO_2) in a given portion. Standards are then prepared by dilution.

Color.—All suspended matter should be removed by filtration. The standard designated as color 500 is obtained as follows:

1.246 grams potassium platinic chloride ($PtCl_4 2KCl$) [1] containing 0.5 gram of platinum and 1 gram of crystallized cobalt chloride ($CoCl_2 6H_2O$) containing 0.25 gram cobalt (Co), are dissolved in water with 100 ml. hydrochloric acid and made to one liter with distilled water. This solution is diluted with distilled water for comparative purposes, but a water with a color greater than 70 should be diluted prior to comparison. The standards for observation should be in 100-ml. Nessler tubes with the mark 20–25 cm. above the bottom and should be viewed vertically downwards to a white reflective surface.

Standard glass disks are used by the United States Geological Survey [2] in place of the above standard.

Odor.—Observations should be made both on cold and hot samples. Note should be made immediately on opening containers as some odors are very transient and rapidly disappear.

Cold.—Shake sample violently in collecting bottle, same to be about half full. Remove glass stopper and smell at neck of bottle.

Hot.—Use either open beaker, 400 ml., containing 150 ml. sample well covered and heated nearly to boiling, or sealed glass stoppered bottle or saponification flask, heating fifteen minutes just under boiling. Allow to cool slightly, remove stopper, shake and smell. Designate odor as aromatic, grassy, earthy, musty, fishy, putrid, disagreeable, peaty, sweetish, etc. The following table expressing intensity of odor is copied from the American Public Health Association Standard Methods, 1913, p. 12:

Numerical Value.	Term.	Approximate Definition.
0	None.	No odor perceptible.
1	Very Faint.	An odor that would not be detected ordinarily by the average consumer, but that could be detected in the laboratory by an experienced observer.
2	Faint.	An odor that the consumer might detect if his attention were called to it, but that would not attract attention otherwise.
3	Distinct.	An odor that would be detected readily and that might cause the water to be regarded with disfavor.
4	Decided.	An odor that would force itself upon the attention, that might make the water unpalatable.
5	Very Strong.	An odor of such intensity that the water would be absolutely unfit to drink. A term to be used only in extreme cases.

[1] Care should be taken that this be the bright yellow platinic salt, and not contaminated with the reddish platinous salt.

[2] App. made by Builders' Iron Foundry, Providence, R. I.

Taste.—May be made on hot and cold samples. A simple statement following largely the terms applied to odor in expressing results, brackish, astringent, salty, sweetish, etc.

CHEMICAL TESTS

Free Ammonia

Apparatus.—The apparatus for this determination should be as far as possible free from joints or connections that are subject in any way to outside contamination or to decomposition. The apparatus is composed of a distillation flask and a condenser, with possibly a safety tube located somewhere near the flask to avoid the possible carrying over of impurities in connection with the steam.

Reagents: 1. *Ammonia-free Water.*

2. *Standard Ammonium Chloride Solution.*—Dissolve 3.82 grams of ammonium chloride in 1 liter of distilled water. Dilute 10 ml. of this to 1 liter with ammonia-free water. 1 ml. = 0.00001 gram of nitrogen.

3. *Nessler's Solution.*—Dissolve 50 grams of potassium iodide in the smallest possible quantity of cold water. Add a saturated solution of mercuric chloride until a faint show of excess is indicated. Add 400 ml. of 50% solution of potassium hydroxide. After same has clarified by sedimentation, make up to 1 liter with water, allow to settle and decant.

Optional Method.—Dissolve 61.75 grams of potassium iodide in 250 ml. of redistilled water, and add a cold solution of mercuric chloride which has been saturated by boiling with excess of salt. Pour in the mercury solution cautiously, and add an amount just sufficient to make the color a permanent bright red. With a little practice the exact depth of color can be easily duplicated. It will take a little over 400 ml. of the mercuric chloride solution to reach this end-point. Dissolve the red precipitate by adding exactly .75 gram of potassium iodide. Then add 150 grams of potassium hydroxide dissolved in 250 ml. of water. Make up to 1 liter. Mix thoroughly and allow the precipitate formed to settle. Pour off the supernatant liquid. Mercuric chloride increases the sensitiveness and potassium iodide decreases it.

Operation.—Clean apparatus thoroughly as follows:

Fill a flask, which for most satisfactory results should be an 800-ml. Kjeldahl flask, with 500 ml. of distilled water. Add a pinch of c.p. sodium carbonate and distill first of all with no running water in the condenser jacket until free steam blows through the apparatus. Then turn on condenser water and distill off approximately 250 ml., testing the last 50 ml. with Nessler's solution, and this portion should not show color in fifteen minutes' time. The flask is then emptied of the remaining water, 500 ml. of the water to be analyzed placed therein, and if acid, neutralized with c.p. sodium carbonate. A slight excess hurries the

ammonia liberation but also tends to cause bumping. The distillation is then started, distilling 6 ml. to 10 ml. per minute, and three separate portions of 50 ml. each are caught in Nessler jars. After 150 ml. is distilled the flame should be removed. To each 50-ml. portion add 2 ml. Nessler's solution and after ten minutes' standing compare with standards from the standard ammonium chloride solution.

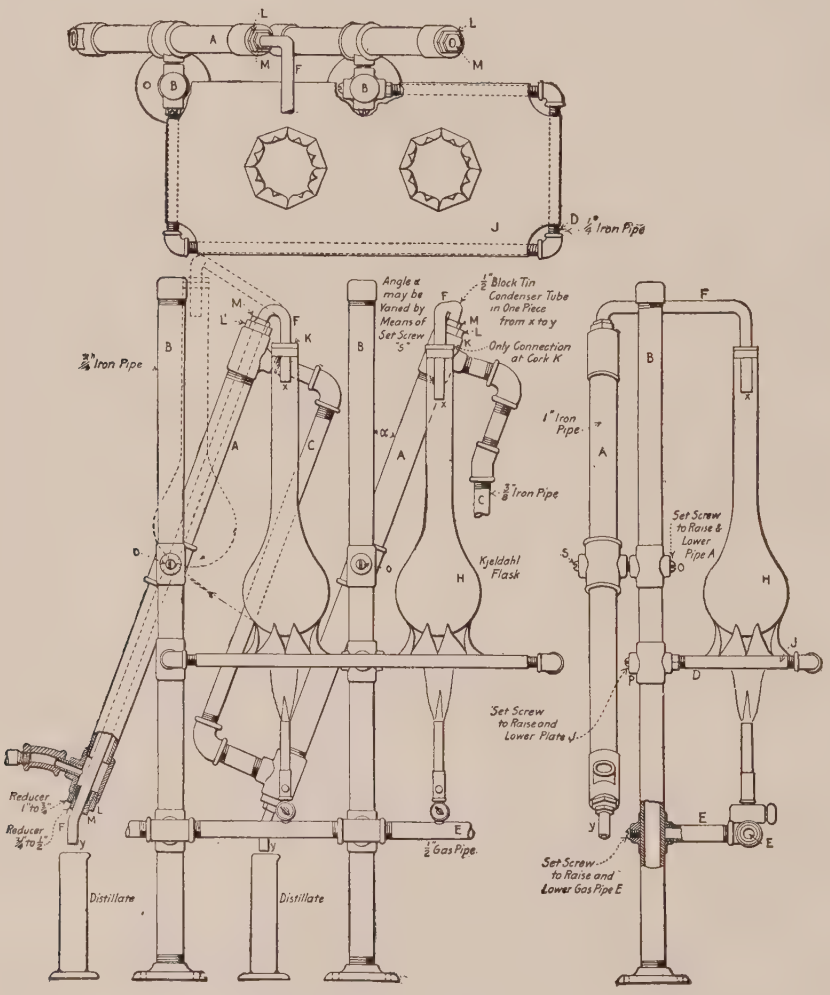

Angle α may be Varied by Means of Set Screw "S"
½" Block Tin Condenser Tube in One Piece from x to y
Only Connection at Cork K
¾" Iron Pipe
1" Iron Pipe
⅜" Iron Pipe
Kjeldahl Flask
Set Screw to Raise & Lower Pipe A
Set Screw to Raise and Lower Plate J
Reducer 1" to ⅜"
Reducer ¼" to ⅛"
½" Gas Pipe
Distillate
Distillate
Set Screw to Raise and Lower Gas Pipe E

FIG. 288.—Free Ammonia Apparatus.

Albuminoid Ammonia

Reagent: 1. ***Alkaline Potassium Permanganate.***—Dissolve 200 grams of potassium hydroxide and 8 grams c.p. potassium permanganate in 1250 ml. of water, boil down to 1 liter and bottle while still warm.

Operation.—Add 50 ml. alkaline potassium permanganate solution and several pieces of washed and ignited pumice to the water remaining in the flask from the free ammonia determination and continue the distillation, taking off four or five separate portions of 50 ml. each in Nessler jars. Add 2 ml. Nessler's solution to each and after ten minutes' standing compare color with standard as in the free ammonia determination.

Organic Nitrogen

While this determination is not usually made we give it for the sake of completeness.

The portion of sample from the free ammonia determination, or a new portion freed from free ammonia by distillation, is acidified with 5 ml. c.p. sulfuric acid (nitrogen-free) and digested in a hood until colorless and H_2SO_4 fumes are given off. A little ignited pumice will guard against bumping.[3] Cool, dilute with ammonia-free water, neutralize with 10% Na_2CO_3 solution (NH_3 free), distill into Nessler tubes and compare as for free and albuminoid ammonia.

Permanent standards [4] can be made by using potassium platinic chloride, 2 grams dissolved in water, 100 ml. conc. hydrochloric acid and made to 1 liter; and cobalt solution, 12 grams cobaltous chloride ($CoCl_2 \cdot 6H_2O$) dissolved in distilled water, 100 ml. conc. hydrochloric acid added and made to 1 liter. The following table represents the amounts used, to be made to 50 ml. with distilled water in Nessler tubes for comparison, the 150-ml. mark being 20–25 cm. above the bottom, but should be checked against Nesslerized standards and the Nessler solution modified, if necessary, until the standards agree. This is accomplished by varying the amounts of potassium iodide and mercuric chloride.

Equivalent Volume of Standard Ammonium Chloride, ml.	Platinum Solution, ml.	Cobalt Solution, ml.
0.0	1.2	0.0
0.1	1.8	0.0
0.2	2.8	0.0
0.4	4.7	0.1
0.7	5.9	0.2
1.0	7.7	0.5
1.4	9.9	1.1
1.7	11.4	1.7
2.0	12.7	2.2
2.5	15.0	3.3
3.0	17.3	4.5
3.5	19.0	5.7
4.0	19.7	7.1
4.5	19.9	8.7
5.0	20.0	10.4
6.0	20.0	15.0
7.0	20.0	22.0

[3] $KMnO_4$ is sometimes used at this point, but as it may cause loss of N, the practice is not advisable.

[4] Permanent Standards (Jackson, Tech. Quart., **13**, 320 (1900)).

Nitrogen as Nitrite

Reagent: 1. ***Sulfanilic Acid.***—Dissolve 8 grams of the acid in 1 liter of acetic acid, specific gravity 1.04. This is practically a saturated solution and keeps well.

2. ***Naphthylamine Acetate.***—Dissolve 5 grams of α-naphthylamine in 1 liter of acetic acid, specific gravity 1.04, and filter through absorbent cotton (previously washed).

NOTE.—A slightly pink color resulting on standing does not materially interfere with the use of this solution.

3. ***Sodium Nitrite Solution.***—Dissolve 1.1 grams of silver nitrite in nitrite-free water. Precipitate the silver with sodium or potassium chloride solution and dilute to 1 liter. Dilute 100 ml. of this solution to 1 liter and then 10 ml. of this second solution to 1 liter with sterilized nitrite-free water, adding 1 ml. of chloroform and holding in a sterilized bottle. 1 ml. = 0.0001 milligram of nitrogen.

Operation.—Take 100 ml. of the water after filtration and clarification, preferably with aluminum hydroxide, to remove possible suspended iron and material which might interfere with color production. Add 2 ml. each of solutions No. 1 and No. 2. After ten minutes' standing compare with standards made up from the standard sodium nitrite solution (No. 3).

PERMANENT STANDARDS

Cobalt Solution.—Dissolve 24 grams of cobaltous chloride ($CoCl_2 \cdot 6H_2O$) in distilled water, add 100 ml. of conc. hydrochloric acid and make up to one liter with distilled water.

Copper Solution.—Dissolve 12 grams of dry cupric chloride ($CuCl_2 \cdot 2H_2O$) in distilled water, add 100 ml. of conc. hydrochloric acid and make up to one liter with distilled water.

The standards are used in 100-ml. tubes with the mark 12–14 cm. above the bottom. The following table gives the proportions of each solution to be made up to 100 ml.:

ml. Cobalt Solution.	ml. Copper Solution.	p.p.m. Nitrite per 100 ml. of Water.
.0	.0	.000
1.1	1.1	.001
3.5	3.0	.003
6.0	5.0	.005
12.5	8.0	.010

The solutions to use for 100 ml. of water are the old ones, as follows: 1 ml. of hydrochloric acid (1 : 4), 2 ml. of sulfanilic acid (8 grams per liter), and finally 2 ml. of naphthylamine hydrochloride (8 grams per liter with 10 ml. of conc. hydrochloric acid), and allow color to develop twenty minutes.

NOTE.—Volume 28, page 742, J. Soc. Chem. Ind., calls attention to the possibility of a permanent standard composed of a solution of acid magenta (fuchsine–S, acid fuchsine according to Weigert). According to this article, 0.2 of a gram of this dye

is dissolved in 50 ml. of 2/N HCl and made up to 2000 ml. with distilled water. Of this solution 200 ml. are mixed with 50 ml. of 2/N HCl and again diluted to 2000 ml. with distilled water. From this latter solution standard solutions can be prepared containing various quantities, these standards being made up to 200 ml. with distilled water after the addition of 5 ml. of 2/N HCl. Considerable work is being done on this, but the standards have not yet been accepted in this country. However, standards can be made by matching these solutions against standards prepared in the usual way and their permanence is much greater than such standards.

Nitrogen as Nitrate

Aluminum Reduction [5]

Reagents: 1. *Sodium or Potassium Hydroxide Solution.*—Dissolve 250 grams of the hydrate in 1250 ml. of distilled water, add several strips of aluminum foil and allow action to pass overnight. Boil down to 1 liter.

2. *Aluminum Foil.*—Use strips of pure aluminum approximately 10 cm. long, 9 mm. wide, and ⅓ mm. thick, same to weigh about ½ gram.

Operation.—100 ml. of water is placed in a 300-ml. casserole. Add 2 ml. of the hydroxide solution and boil down to about 20 ml. Pour the contents of the casserole into a test-tube about 3 cm. in diameter and of approximately 100-ml. capacity. Rinse the casserole several times with nitrogen-free water and add the rinse water to that already in the tube, thus making the contents of the tube approximately 75 ml. Add a strip of aluminum foil. Close the tube by means of a rubber stopper through which passes a Λ-shaped glass tube about 5 mm. in diameter. Make the short end of the tube flush with the lower side of the rubber stopper while the other end extends below the surface of distilled water contained in another test-tube. This apparatus serves as a trap through which the evolved hydrogen escapes freely. The amount of ammonia escaping into the trap is slight and may be neglected. Allow the action to proceed for a minimum period of four hours, or overnight. Pour contents of the tube into a distilling flask, dilute with 250 ml. of ammonia-free water, distill and collect in Nessler tubes and Nesslerize. When the nitrate content is high, collect the distillate in a 200-ml. flask and Nesslerize an aliquot portion. If the supernatant liquid in the reduction tube is clear and colorless, the solution may be diluted to a definite volume and an aliquot part Nesslerized without distillation.

Note.—Where the nitrates are very high, from 50 parts per million up, take a smaller sample and dilute to 100 ml. before reduction.

Oxygen Consumed

Reagents: 1. *Standard Potassium Permanganate Solution.*—Dissolve 0.4 gram c.p. salt in 1 liter of distilled water. 1 ml. is equivalent to 0.1 milligram available oxygen.

2. *Standard Ammonium Oxalate Solution.*—Dissolve 0.888 gram c.p. ammonium oxalate in 1 liter of distilled water. 1 ml. is equivalent to 0.1 milligram of oxygen. The standard permanganate solution must be standardized against the ammonium oxalate solution.

[5] Univ. of Illinois Bull. Water Survey, Series 7, p. 14 (1909); Amer. Jour. Pub. Hygiene, **19**, 536 (1909).

3. *Dilute Sulfuric Acid 1:3.*—Free from oxidizable matter by adding $KMnO_4$ until a faint pink color persists after several hours.

Operation.—100 ml. of water are measured into a 450-ml. Erlenmeyer flask, acidified with 5 ml. dilute sulfuric acid. Ten ml. of standard permanganate solution is run in from a burette and the flask is placed in a bath of boiling water, the level of which is above the level of the flask contents, for thirty minutes. Remove. Add 10 ml. of standard oxalic solution and then determine the excess with the standard permanganate solution. Deduct from the total permanganate solution used the 10 ml. of oxalic acid, and the remainder represents oxygen consumed. For particularly bad waters smaller quantities of the sample are taken and diluted to 100 ml., as it is undesirable at any time in the course of boiling that the pink color of permanganate be completely discharged.

Chlorine as Chlorides

Reagents: ***Standard Salt Solution.***—16.48 grams fused c.p. sodium chloride are dissolved in 1 liter of distilled water. 100 ml. of this solution diluted to 1 liter gives a standard solution, each ml. of which contains .001 gram of chlorine.

Standard Silver Nitrate Solution.—4.8 grams dried silver nitrate crystals are dissolved in one liter of distilled water. Each ml. of this solution is equivalent to approximately .001 gram of chlorine, standardized against the Standard Salt Solution.

Note.—N/50 solutions of both sodium chloride and silver nitrate can be used where it is inconvenient to make too many standard solutions, using the proper factors.

Potassium Chromate.—10% solution neutral potassium chromate.

Note.—A. P. H. A., page 35, recommends 5% solution of neutral potassium chromate, adding after solution of the crystals in a few ml. of water, sufficient silver nitrate to produce a slight red precipitation. This is filtered off, and the filtrate made up to volume.

Operation.—100 ml. of the sample are titrated with silver nitrate solution, using 1 ml. of the potassium chromate as indicator to the first persistence of the silver chromate red. Subtract 0.2 ml. blank from the reading. A white porcelain dish or casserole is the preferable container, although a flint-glass beaker over a white porcelain plate may be used. Where a chlorine is high and more than 15 ml. of silver is used, a smaller sample (50 ml. or 25 ml.) should be taken and distilled water added to bring the volume up to approximately 100 ml. If the original water is noticeably colored, 25 to 30 by standard, it may be decolorized by adding precipitated aluminum hydroxide, bringing to a boil and filtering. Titration must always be made in the cold, however.

Note.—Precipitated aluminum hydroxide is prepared by dissolving potash alum in water, precipitating by adding carefully ammonia and washing in a large jar with distilled water, by decantation, until free from chlorine, ammonia, and nitrites. An acid water should first be neutralized with sodium carbonate and a water containing free hydroxides should be neutralized with sulfuric acid. Where specially accurate work is desired, observations may be made in a dark room with a yellow light. (A. P. H. A., page 36.) A yellow photographic glass may be used in daylight and at night the ordinary carbon filament electric light.

Total Solid Residue

Evaporate 50 ml. to dryness, in a platinum dish, at about 270° Fahr., and bake for at least 30 minutes at that temperature. An ordinary water-bath temperature will not remove water of crystallization from alkali sulfates or calcium sulfate. Where water is high in magnesium salts, as determined in mineral analysis, the water-bath temperature is more satisfactory, due to the readiness with which magnesium chloride and frequently magnesium carbonate will decompose to oxide. As a rule, however, a temperature from 240° to 270° meets most of the conditions.

Weight in grams times 1168 = grs. per gal. total solids.
Weight in grams times 20,000 = parts per million total solids.

Residues from acid waters should be ignited to a dull red heat after addition of a drop or so of sulfuric acid, to insure complete removal of the acid itself, which will not go off at the temperature stated. This will result in the decomposition of all iron compounds to the oxide form, and will fix all salts, lime, magnesium, sodium and potassium, in the sulfate form, and correction should be made for chlorides present, which would be converted into sulfates.

Waters high in magnesium salts should be evaporated at the first specified temperature, adding, however, a few ml. of N/50 normal sodium carbonate solution to insure a slight excess of sodium carbonate, correcting for the weight of sodium carbonate added. Where the waters contain much organic matter after weighing, they may be very gently ignited at a very dull red heat until the carbon has been burned off. After cooling, the residue may be recarbonated with tested ammonium carbonate solution, and again dried in the usual way. The difference in weight after titrating for possible loss of chlorides, due to volatilization, gives a close approximation of the organic matter present. Similarly, waters high in magnesium chloride or nitrate compounds may be evaporated with a few drops excess of sulfuric acid, and ignited to a dull red heat, the residue being compared, where a complete analysis is made, with the sum of all bases calculated to the sulfate form. This is sometimes more convenient and satisfactory than the evaporation with excess sodium carbonate.

INTERPRETATION OF RESULTS

The interpretation of the results of a sanitary water analysis is largely a matter of experience, and it is impossible to lay down hard and fast rules covering this one matter. It is, however, possible to sum up the meanings of the various determinations made, as each determination has some bearing upon the sanitary condition.

In physical data the turbidity refers to insoluble matter in suspension. In many cases it is perfectly harmless, although less attractive, and frequently

suggests contamination, which is as apt to be present as not. High turbidities, following rain storms or lake over-turnings, are usually accompanied by B. coli, the intestinal organism, in considerable quantity. The turbid waters of the West may cause stomach trouble until a person is accustomed to them. Color is due, usually, to an extract of vegetable or organic matter, or to iron salts, and in itself has no value save suggesting organic contamination. Highly colored water may have an astringent taste, and is not looked upon with favor by the consumer. It may cause corrosion in pipes and boilers.

Various organic matters are in no way determined in this analysis, the results obtained being simply indications of certain cycles in decomposition of nitrogenous material, as no decomposition can take place without some resulting nitrogen compound. Free ammonia represents the first stage in this decomposition, and represents the amount of organic matter present in a partially decomposed and decomposing state. Deep wells in glacial drift frequently also contain high ammonia, however, which would in no way suggest active contamination.

Albuminoid ammonia represents organic substances in an undecomposed state, which will, however, decompose under the proper conditions. The presence of nitrogen in such combination in large amount usually suggests the presence of pollution of a sewage character. However, its presence usually accompanies and varies in amount with the color and with the microscopic organisms.

The next stage in the cycle is nitrogen as nitrites, indicating that decomposition is actively progressing. Nitrite in surface water may indicate contamination when in considerable quantity, but in ground water is absolutely of no significance. (Proc. Am. W. W. Assoc., 1908, page 323.) Its presence is due to the action of certain types of bacteria either as a product of oxidation from free ammonia or as a product of reduction from nitrate. Ferrous compounds have also a bearing on such reduction.

The final state of decomposition is nitrogen as nitrate. This indicates the fact that at some time in the past organic matter has been present. Its presence indicates a purified water. In large amounts it may cause itching in sensitive persons. It is an important cause of corrosion in pipes and boilers.

The oxygen consumed represents the amount of oxygen required to oxidize organic matter already in the water. It has a bearing upon the organic matter, but there are many inorganic substances which also discharge the color of the permanganate solution, and the result should always be considered in the presence of the other determinations.

Chlorine as chlorides, if above the normal figure for any definite location, is a fairly good indication of sewage, as it is one of the most constant and principal constituents of sewage.

The total residue itself should not be too high, as an excess of inorganic materials would stamp the water unfit from an industrial point of view, and also, from the standpoint of the individual, might make it unsatisfactory as a drinking supply for daily consumption.

With reference to standards of purity, it is impossible to make absolute standards. We quote as a matter of interest a table published by the State of Illinois, giving their suggested limits of impurities for supplies in that State. (The remarks which follow are those of the State Geological Survey.)

	Lake Michigan.	Streams.	Springs and Shallow Wells.	Deep Drift Wells.	Deep Rock Wells.
Turbidity	None	10.	None	None	None
Color	None	.2*	None	None	None
Odor	None	None	None	None	None
Residue on Evaporation	150.	300.	500.	500.	500.
Chlorine	4.5	6.	15.	15.	5.–100
Oxygen consumed	1.6	5.	2.	2.–5	2.–5
Nitrogen as:					
Free Ammonia	.01	.05	.02	.02–3	.02–3
Albuminoid Ammonia	.08	.15	.05	.20	.15
Nitrites	.000	.000	.000	.005	.000
Nitrates	.04	.5	2.00	.5	.5
Alkalinity	120.	200.	300.	300.	300.
Bacteria per ml	100.	500.	500.	100.	100.
Colon bacillus in one ml	Absent	Absent	Absent	Absent	Absent

* Modified Nessler or Natural Water Standard equal 26 p.p.m. platinum scale.

The formation of a reasonable and just opinion regarding the wholesomeness of a water requires that there be taken into consideration all the data of the analysis, together with the history of the water; the nature of the source; character of the soil and earth or rock strata, and the surroundings. The interpretation of results is a task for the expert. If possible a bacteriological examination should be made to supplement the sanitary analysis, as the latter is more useful in determining the source of pollution and indicating the stage of contamination.

Chlorine is the most permanent element shown in water analysis, as it is never removed from water by any changes or processes of purification. Salt deposits, however, in the soil must also be taken into consideration.

MINERAL ANALYSIS

Outline of Procedure

Evaporate 50 ml. of the sample of water to dryness and bake the residue at 270° F. in weighed platinum dish. Increased weight of dish represents ***total solid residue.*** (Can be used for SO_4 when sample is small.) Ignite for organic loss.

250 ml. Titrate with N/10 acid or alkali for ***alkalinity or acidity.*** (Can be re-used to make up volume of 500-ml. portion when water sample is small.) Methyl orange indicator. (With a 50 ml. sample use N/50 acid.)

100 ml. Titrate with N/10 $AgNO_3$ for ***chlorine.***

100 ml. Acidify, boil, precipitate with $BaCl_2$, filter and weigh for ***total sulfate.*** (Use filtrate for Na and K when necessary.)

100 ml. Add 2 ml. 10% Na_2CO_3, evaporate to dryness, add phenolsulfonic acid, dilute, then excess of NH_4OH for ***total nitrate.***

500 ml. Evaporate to dryness (with a few ml. concentrated HCl when very accurate SiO_2 figure is necessary) in No. 8 R. B. dish. Bake 30 minutes, cool, add boiling HCl (concentrated), dilute and filter.

<table>
<tr><td rowspan="3">Precipitate is SiO_2 and silicate impurities (also $BaSO_4$). Unless great accuracy is necessary, it should be weighed as such, otherwise SiO_2 can be removed by HF and correction made.</td><td colspan="3">Filtrate. Add a few drops of HNO_3, concentrate to 50 ml., cool, add NH_4OH, boil and filter.</td></tr>
<tr><td rowspan="2">Precipitate (Fe, Al, $PO_4^{\equiv}$) may be reported as such or as Fe and Al after Qual. test for phosphate has shown same to be absent. Otherwise both Fe and $PO_4^{\equiv}$ should be determined and weight corrected.</td><td colspan="2">Filtrate. Boil and add saturated Am. Oxalate drop by drop, boil and filter.</td></tr>
<tr><td>Prec. Ca as oxalate. Dissolve in 2% H_2SO_4. Titrate with standard $KMnO_4$.</td><td>Filtrate Mg (and Mn), add 10–25 ml. concentrated Sod. Phos. Solution, then 50 ml. NH_4OH, stir well 2 minutes, or more, let stand 4 hours, or more, filter and wash with 3% NH_4OH. Dry in air oven at 50°–60° C. Add excess N/10 H_2SO_4 to dissolve ppt. Titrate the excess acid with N/10 NaOH.</td></tr>
</table>

NOTE.—For industrial purposes the original addition of HCl is not always necessary and correction for $BaSO_4$, Phos. Mn and separation of Fe and Al can be dispensed with unless there is cause to suspect one to be present in material amounts.

In the matter of mineral analysis of water, it is not so hard to obtain a complete analysis of the water, including the non-incrusting or "nearly always" soluble materials as well as the incrusting materials, as it is to make numberless individual or independent tests, in the hope of drawing conclusions from same. The scheme of analysis which follows is used exclusively in the writer's laboratories, and when carried out as given, makes it possible to complete analysis of a water, or a group of waters numbering up to ten, in the period of eight hours elapsed time, or twenty-four hours, assuming the work is arranged in such a way that the magnesia precipitates are allowed to stand overnight before filtration. On another page will be found a skeleton form for this complete analysis, and this skeleton will serve as a rough guide to the more extended discussion which will follow.

The complete analysis considers the quantitative determinations of silica, iron and aluminum, calcium, magnesium, sodium and potassium, as bases, and carbonate, hydroxide, nitrate, sulfate, chloride, and phosphate, as radicals or

acids, with suggested methods for manganese, ammonia, barium, and other materials which might possibly be present.

Prior to the starting of the analysis, the physical characteristics of the water should be noted, turbid waters should be filtered, the suspended matter analyzed separately when necessary, and the amount determined either by filtration and weighing of the separated material (alundum cones are very satisfactory), or by the difference between two residues, one of which represents the original water and one the filtered water. The mineral analysis should represent the filtered supply. This is due to the difficulty of getting uniform samples with suspended matter at different times. Treatment with H_2O_2 is also sometimes effective when the color is high.

NOTE.—Due to the tendency of some grades of H_2O_2 to change both alkalinity and chloride figures, the material used should be examined carefully. Merck's Super Oxol (30% H_2O_2) has been found thoroughly satisfactory and has not affected analytical results.

Silica, Iron, Aluminum, Calcium, Magnesium

(Manganese, Phosphoric Acid)

NOTE.—If from qualitative observations the water contains considerable mineral matter, smaller quantities varying from 100 to 250 ml. may be taken, or if the sample is apparently distilled or condensed and contains very little mineral matter, 1000 ml. should be taken, the object being to obtain a residue neither too large nor too small. 0.4 to 0.6 gram is a good quantity to work on.

Silica

Add 5–10 ml. HCl, evaporate over free flame, then on ¼-in. asbestos board, to dryness, 500 ml. original water, using a No. 8 porcelain dish. Bake at 110°–130° C. or on asbestos plate over flame for one-half hour. Moisten with 10 ml. concentrated HCl, add 50 ml. of water, boil fifteen to thirty seconds and filter. Wash with hot water.

NOTE.—For great accuracy, evaporate twice to dryness as above, with the addition, prior to the sample going to dryness, of 10 ml. HCl, allow to bake as above, following from there on the usual procedure for filtration.

NOTE.—When the water is highly colored due to organic matter, a few ml. of HNO_3 can also be added.

The precipitate retained on the filter paper represents the silica or siliceous matter, including possibly barium sulfate. Ignite and weigh.

NOTE.—If the amount is over .01 g. per liter, or 10 parts per million, moisten with a few drops of concentrated sulfuric acid and hydrofluoric acid, expel excess acids, and reweigh. This must be done in platinum. The loss represents silica, and should be recorded as such, and the residue represents bases, principally barium, combined with sulfuric acid. This will also catch possible calcium sulfate that might be left undissolved, due to short boiling, to low dilution, or conditions which would prevent its normal solubility in the original solution.

NOTE.—When a large amount of $CaSO_4$ is suspected or indicated, extra care must be taken to remove it completely by solution.

Iron and Aluminum (Gravimetric)

The filtrate contains iron, aluminum, calcium, magnesium, possibly manganese, and phosphate. Bring to a boil, add two or three drops conc nitric acid

and concentrate to about 25–50 ml. Remove from hot plate or flame, add ammonium hydroxide in slight excess, boil for one or two minutes, and filter.

The precipitate contains iron, aluminum, and possibly phosphates. Burn and weigh as oxides of iron and aluminum, plus phosphates, and test 50 ml. of the original water with treatment in the usual way to determine whether or not phosphates are present. Where this precipitate of iron and aluminum oxides is greater than 0.01 g. per liter or 10 parts per million, or where the separation of the iron and aluminum is advisable, the precipitate should be fused with eight or ten times its weight of potassium bisulfate, redissolved in water, the iron reduced to the ferrous condition with zinc, and titrated with potassium permanganate, recording the difference in weight between the original precipitate and the iron determination as aluminum oxide.

$$Fe \times 1.43 = Fe_2O_3.$$

NOTE.—Where much water is available and time is an object, an additional 500 ml. can be carried down to approximately 50 ml. with a few drops of nitric acid, the iron and aluminum precipitated as above mentioned with ammonia, and the precipitate before drying redissolved in acid, reduced and titrated with potassium permanganate. This portion can be started at the same time the original analysis is started, and will greatly simplify the determination and save time.

Total Iron (Colorimetric)

Reagents: ***Iron Standard.***—0.7 g. cryst. ferrous ammonium sulfate is dissolved in a small amount of distilled water, add 25 ml. dilute (1:5) sulfuric acid, warm slightly and oxidize completely with potassium permanganate, make up to 1000 ml. 1 ml. = 0.1 mg. Fe.

Potassium Sulfocyanide.—2% solution.

Potassium Permanganate.—6.3 g. per liter.

Operation.—Instead of precipitating, or where *traces* of Fe are of importance, 100 ml. to 1000 ml. of the water may be carried to dryness with HCl and a few drops of Br, taken up with 5 ml. (1 : 1) HCl, diluted to 100 ml. in a Nessler tube, 10 ml. KCNS solution (20 g. to a liter) added and the color compared with standards. The comparison should be made at once as the color fades.

NOTE.—It is frequently as satisfactory to add the standard iron solution from a burette to a 100 ml. Nessler tube containing 5 ml. (1 : 1) hydrochloric acid (Fe free), 10 ml. potassium sulfocyanide solution (20 g. to a liter) and sufficient distilled water until the color matches that of the sample.

(Ferrous Iron—Colorimetric)

(Frequently desirable in acid waters but rarely necessary.)

Reagents: ***Iron Standard.***—0.7 g. cryst. ferrous ammonium sulfate is dissolved in one liter of distilled water containing 10 ml. dilute H_2SO_4. (Not permanent. Should be made up as needed.) 1 ml. = 0.1 mg. Fe.

Potassium Ferricyanide Solution.—(Prepare as needed.) 0.5 g. per 100 ml. distilled water.

Sulfuric Acid.—1 : 5.

NOTE.—Prepare sample and standards at same time.

Operation.—Place in 100 ml. Nessler jar 50 ml. of sample, 10 ml. dilute H_2SO_4 (1:5), filter, if necessary, to remove suspended matter, add 15 ml. potassium ferricyanide solution and make up to 100 ml. mark with distilled water. Compare with standards made as follows:

Place in 100 ml. Nessler jar 75 ml. distilled water, 10 ml. dilute H_2SO_4 (1:5) and 15 ml. potassium ferricyanide solution, and mix well. Add various amounts of iron standard from burette, mix and compare color. Determine ferric iron by deduction of ferrous iron from total iron.

Phosphates

Reagents: ***Ammonium Molybdate.***—50 g. c.p. neutral salt dissolved in 1 liter distilled water.

Nitric Acid (spec. grav. 1.07).—Dilute about 1:5 with distilled water.

Standard Phosphate Solution.—0.5045 g. c.p. cryst. $Na_2HPO_4 \cdot 12H_2O$. Dissolve in distilled water, 100 ml. standard HNO_3 added. Dilute to 1 liter.

One ml. = 0.0001 gram P_2O_5.

Operation.—Evaporate 50 ml. water to dryness in porcelain after addition of 3 ml. HNO_3 (spec. grav. 1.07). Bake two hours at 212° F. Take up with 50 ml. distilled water, add 4 ml. molybdate solution and 2 ml. HNO_3, and compare in Nessler tube with standards from phosphate solution made to 50 ml. and treated with same reagents. A tube 2.5 cm. by 24 cm. to 100-ml. mark of hard, white glass is most suitable.[6] Where waters are already colored the evaporation should be carried on with 3 ml. HNO_3 and 0.5 ml. (or more, if water is highly colored) of $KMnO_4$ solution (1 gram per 1000 ml.), baking at 212° F. for the same time.[7] Where the phosphate is present in large enough quantities to precipitate the gravimetric methods may be used.

Calcium

The filtrate from iron, aluminum and phosphate precipitate contains calcium, magnesium, and possibly manganese. Concentrate to about 100 ml. Add to the hot ammoniacal solution a saturated solution of ammonium oxalate drop by drop, or add in small portions crystals of ammonium oxalate. Allow to boil two minutes, stirring, if necessary (on account of heavy precipitate and tendency to bump), remove, filter and wash. (Eight complete washings are usually sufficient.)

Note.—Where great accuracy is desired, the precipitate on the filter should be redissolved in a small amount of hot, dilute, hydrochloric acid and reprecipitated with ammonium oxalate.

Dissolve in 2% sulfuric acid and titrate with the standard solution of potassium permanganate. (N/50 $KMnO_4$ may be used.)

Note.—Where the volumetric method is to be used, eight complete washings are, as a rule, sufficient to remove the traces of ammonia salts, which are prone to have considerable influence upon the volumetric results, due to the possibility of traces of ammonium oxalate still being present.

[6] J. Am. Chem. Soc., **23**, 96 (1901).
[7] J. Ind. Eng. Chem., **5**, 301–2 (1913).

Fe Value $\times 0.896 = CaCO_3$.
Fe Value $\times 0.5021 = CaO$.
Fe Value $\times 0.3589 = Ca$.

Optional (Gravimetric)

Instead of redissolving and titrating the calcium oxalate upon the filter paper, it can be dried, burned and weighed either as calcium oxide or calcium carbonate.

NOTE.—The burning of calcium oxalate to carbonate is not so difficult as it seems, as an intense heat is necessary to convert it to the oxide, and if the crucible is well watched and the flame gives just sufficient heat to carbonize and destroy the filter paper, there will be no chance whatever of any calcium oxide being formed, or any calcium oxalate being left. Where hypothetical combinations are used, it is very convenient to have the calcium as carbonate without calculation. Where burned to the complete oxide it is frequently necessary to use a blast lamp, as large precipitates require a high temperature to reduce completely to oxide form.

Magnesium

The filtrate contains magnesium (*and possibly manganese*). Acidify with HCl, concentrate if necessary to 150 ml., add 25 ml. saturated solution of ammonium sodium hydrogen phosphate ($NH_4NaHPO_4 \cdot 4H_2O$, microcosmic salt), cool and make alkaline with ammonium hydroxide. Allow to stand at least four hours.

The precipitate is washed several times by decantation with ammonium hydroxide solution (1 part NH_4OH, sp.gr. 0.90 to 9 parts water), and finally on the filter. After draining, the filter paper is opened out, the moisture removed as much as possible by means of dry filter paper. The residue may be dried in the room for about forty-five minutes or in the air oven at 50° to 60° C. for fifteen to twenty minutes. When the filter has dried, ammonia will have been expelled. Entire paper, etc., is placed in a dry beaker, N/10 sulfuric acid added in excess, using the methyl orange indicator, the solution diluted to 100 ml. and the excess of acid titrated with N/10 sodium hydroxide.

One ml. N/10 $H_2SO_4 = 0.00216$ gram MgO.

NOTE.—Accurate results are also obtained with the use of sodium phosphate added direct to the filtrate from the calcium precipitate without previously acidifying with acid, with 25 ml. to 50 ml. of ammonium hydroxide added to make strongly alkaline, after which the solution should be very thoroughly stirred (for at least two minutes), using a rubber-ended glass rod. Allow to stand at least four hours.

For very rapid work in either case, if the magnesium solution after the precipitation is cooled in ice-water, filtration can be frequently made in two hours' time.

For extremely accurate work the precipitate produced in either of the methods above should be redissolved in a little dilute HCl and the precipitation repeated.

Optional (Gravimetric)

The ppt. can be filtered, and washed with 3% solution of ammonium hydroxide. Burn and weigh as $Mg_2P_2O_7$.

Optional (Volumetric)

The following method is purely volumetric. It is used in a great many water softening plants for control, is accurate and extremely simple. It is not

used in the general scheme of analysis because it starts with the raw water and not a concentrated sample. A Mg determination can be made in half an hour or less.

Solutions: (1) ***Lime Water.***—A saturated solution is made by shaking an excess of lime with a suitable volume of water. After settling, the clear liquid is siphoned into a bottle. Changes in temperature may cause slight precipitation in the saturated solution. To avoid this it is a good plan to add 10–20 ml. of distilled water per liter of solution.

(2) ***Standard Acid.***—N/50 H_2SO_4.

Procedure.—100 ml. is measured into a 250 ml. volumetric flask, neutralized with H_2SO_4 to methyl orange end point. The liquid is boiled down to about 50 ml. and to the hot solution 50 ml. of lime water added. The flask is filled to the mark with CO_2 free water, plus 5 ml. Place on a steam bath for 10 minutes, cool, allow to settle, pipette out 50 ml. and titrate with N/50 H_2SO_4 using phenolphthalein indicator.

The relation between the lime water and the standard acid is determined by running a blank. This figure once obtained can be used until the lime solution is all used. It is necessary to run blanks on all freshly made lime solutions. It is good practice to check the lime figure from time to time.

Blank $-5\times$ml. acid used = ml. used to ppt. Mg.
This figure $\times 2.4$ = p.p.m. of Mg.

Manganese

Where necessary, manganese should be determined separately in another portion of the water and corrections made. The Knorres Persulfate method is the most reliable for large amounts (10 milligrams Mn per liter); the Bismuthate method for smaller amounts.

Knorres Persulfate Method (Volumetric)

Reagents: ***Potassium Bisulfate*** c.p.

Ammonium Persulfate Solution (60 grams per liter distilled water).

Hydrogen Peroxide Solution.—Equivalent to N/10 $KMnO_4$. (Approx. 5.6 ml., 3% H_2O_2 diluted to 100 ml.)

Operation.—Evaporate 5 liters or more to dryness, adding first 10 ml. concentrated H_2SO_4. Ignite after adding a few crystals of potassium bisulfate and take up in hot water. Transfer to 250-ml. Erlenmeyer flask with 5 ml. dilute (1 : 3) H_2SO_4, add 10 ml. ammonium persulfate solution, boil twenty minutes, cool, dissolve precipitate (manganese superoxide) in standard hydrogen peroxide solution. (If no ppt. forms no manganese is present.)

Notes.—When hydrogen peroxide solution is standardized against N/10 $KMnO_4$ 1 ml. will be equivalent to 2.747 milligram Mn.

An excess of 10–20 ml. H_2O_2 solution can be added and this excess titrated with N/10 $KMnO_4$.

Sodium Bismuthate Method (Colorimetric) [8]

Reagents: ***Potassium Permanganate.***—0.288 gram $KMnO_4$ to 1000 ml. 1 ml. = 0.1 milligram Mn.

[8] J. Am. Chem. Soc., 29, 1074–78, 1907.

Sodium Bismuthate (purest).

See method of preparation of reagent given on page 1198.

Nitric Acid.—(Spec. grav. 1.135) 3 parts concentrated HNO_3 to 1 part H_2O should be blown with air until free from oxides of nitrogen.

Sulfuric Acid.—25 ml. concentrated H_2SO_4 to 1000 ml. Add permanganate solution to a faint but noticeable color.

Operation.—Evaporate 500 ml. in porcelain dish after adding 1 ml. dilute H_2SO_4 in excess of that necessary to neutralize all alkali. Ignite to remove free acid (organic matter and chlorine), cool and dissolve in 50 ml. HNO_3 (30 ml. concentrated HNO_3 to 1 liter), with heat if necessary. Cool again, add 0.5 gram sodium bismuthate and heat until pink color disappears, re-cool and add sodium bismuthate in excess, filter through asbestos in Gooch crucible (asbestos must be free from organic matter, thoroughly washed and ignited), or alundum crucible. Wash with nitrite-free distilled water containing 5% dilute HNO_3 (30 ml. concentrated HNO_3 per liter). into Nessler tube, make up to 100 ml. and match with color produced by necessary amount of standard $KMnO_4$ in 100 ml. H_2SO_4 reagent.

No. ml. standard $KMnO_4 \times 0.2 =$ milligrams Mn per liter.

Note.—The permanganate solution used for oxygen consumed (see Sanitary Method) contains 0.139 gram Mn per liter and may be used when necessary.

No. ml. $\times 0.278 =$ milligram Mn per liter.

Sulfates

100 ml. of the water is slightly acidified with conc. HCl and 5 ml. 10% NH_4Cl solution added, brought to a boil, and if turbid is filtered and washed four or five times with boiling water. The clear or original water is now brought to a boil and 10% barium chloride added drop by drop to the boiling solution in slight excess. Boil ten minutes, stirring from time to time, if the precipitate is heavy. Remove and *allow to cool* prior to filtering. The precipitate consists of barium sulfate. Wash free from chlorides, testing with $AgNO_3$. Dry, ignite and weigh.

$$BaSO_4 \times .411 = SO_4.$$
$$BaSO_4 \times .583 = CaSO_4.$$

milligrams $BaSO_4 \times .340 = CaSO_4$ grains per gallon.

Benzidine Method (Optional) [9]

Reagents: ***Benzidine Solution.***—Triturate in a mortar with 5 ml. to 10 ml. water, 4 grams benzidine base. Transfer to liter flask, add 10 ml. HCl and make to volume. 1 ml. = .002186 gram SO_4.

Hydroxylamine Hydrochloride.—1% solution in water.

Operation.—Add 10 ml. hydroxylamine hydrochloride to 250 ml. water, then add, at once stirring well, 100 ml. benzidine solution. Allow to stand fifteen to twenty minutes, decant through vacuum filter and wash with 10 ml. to 20 ml. distilled water (do not let filter run dry), return filter paper to beaker, cover with distilled water, bring to a boil and titrate with N/10 or N/50 NaOH, using phenolphthalein as indicator.

[9] Friedheim and Nydegger, Z. angew. Chem., **20**, 9 (1907).

One ml. N/10 NaOH = .0048 gram SO_4.
One ml. N/50 NaOH = .00096 gram SO_4.

N. B. Method by Muer, J. Ind. Eng. Chem., **3**, 553 (1911). When the sulfate is 25 p.p.m. or more, the determination may be made by the turbidimeter method direct on 100 ml. For less quantities, larger amounts of water are taken and evaporated.

Sodium, Potassium and Lithium

Sodium and Potassium

The filtrate contains sodium and potassium and lithium, and may be used for such unless the water is highly mineralized, in which case *a new portion, 100 ml. to 500 ml., should be taken.*

Evaporate to dryness, add saturated solution of barium hydroxide in excess, filter, wash with hot water, add to the filtrate ammonium carbonate in excess and a few drops of ammonium oxalate, boil, filter, evaporate again to dryness and dry at a high temperature to expel excess of ammonia salts. Redissolve, add slight excess of ammonium carbonate again and continue until no further precipitate is formed on such addition. Evaporate to dryness in a weighed platinum dish, remove ammonium salts by high-temperature drying, and weigh the combined chlorides of sodium and potassium. Moisten with about 25 ml. of water and a few drops of HCl and add from 1 ml. to 5 ml. of 10% solution of platinic chloride (1 ml. to each 25 milligrams to 30 milligrams total chlorides). Evaporate to dryness on water bath, take up and wash with 95% alcohol until filtrate is free from color. Dry, redissolve precipitate, washing through the filter paper in hot water. Evaporate again to dryness and weigh as K_2PtCl_6.

$K_2PtCl_6 \times .161 = K.$
$K_2PtCl_6 \times .307 = KCl.$

Deduct from combined weight of chlorides. Remaining $NaCl \times .394 = Na.$

NOTE.—When separation is not necessary, the combined chlorides are calculated as sodium chloride and reported as sodium and potassium chlorides.

See pp. 878–881 for direct methods for Sodium.

Lithium [10]

Use a large quantity of the sample. Obtain the combined chlorides of sodium, potassium and lithium. Transfer the combined chlorides to a small Erlenmeyer flask (50 or 100-ml. capacity) and evaporate the solution nearly, but not quite, to dryness. Add about 30 ml. of redistilled amyl alcohol. Connect the flask, the stopper of which carries a thermometer, with a condenser [11] and boil until the temperature rises approximately to the boiling point of amyl alcohol (130° C.), showing that all the water has been driven off. Cool slightly and add a drop of hydrochloric acid to convert small amounts of lithium hydroxide to lithium chloride. Connect with the condenser and continue the boiling to drive off again all water and until the temperature reaches

[10] See Standard Methods of Water Analysis. A. P. H. A. (1920), page 60.

[11] The amyl alcohol may be boiled off without the use of a condenser, but the vapors are very disagreeable.

the boiling point of amyl alcohol. The content of the flask at this time is usually 15 to 20 ml. Filter through a small paper or a Gooch crucible into a graduated cylinder and note exact quantity of filtrate, which determines the subsequent correction. Wash the precipitate with small quantities of dehydrated amyl alcohol. Evaporate the filtrate and washings in a platinum dish to dryness on the steam bath, dissolve the residue in water, and add a few drops of sulfuric acid. Evaporate on a steam bath and expel the excess of sulfuric acid by gentle heat over a flame. Repeat until carbonaceous matter is completely burned off. Cool and weigh the dish and contents. Dissolve in a small quantity of hot water, filter through a small filter, wash, and return filter to dish, ignite and weigh. The difference between the original weight of dish and contents and the weight of the dish and small amount of residue equals the weight of impure lithium sulfate. The purity of the lithium sulfate should be tested by adding small amounts of ammonium phosphate and ammonium hydroxide, which will precipitate any magnesium present with the lithium sulfate. Any precipitate appearing after standing over night should be collected on a small filter and weighed as magnesium pyrophosphate, calculated to sulfate, and subtracted from the weight of impure lithium sulfate. From this weight subtract 0.00113 gram for every 10 ml. of amyl alcohol filtrate exclusive of the amyl alcohol used in washing residue because of the slight solubility of solid mixed chlorides in amyl alcohol. Calculate lithium from the corrected weight of lithium sulfate. Dissolve the mixed chlorides from flask and filter with hot water, evaporate to dryness, ignite gently to remove amyl alcohol, filter and thoroughly wash; concentrate the filtrates and washings to 25 to 50 ml.

To the weight of potassium chloride add 0.00051 gram for every 10 ml. of amyl alcohol used in the extraction of the lithium chloride, which corrects for the solubility of the potassium chloride in amyl alcohol. Calculate to potassium.

The weight of sodium chloride is found by subtracting the combined weights of lithium chloride and potassium chloride (corrected) from the total weight of the three chlorides. Calculate sodium chloride to sodium.

Alkalinity

In ordinary cases titrate with N/10 or N/50 H_2SO_4, using methyl orange as indicator. Special cases will be considered later.

Reagents.—Sulfuric acid, N/10. Methyl orange. Phenolphthalein.

Operation.—250 ml. of water in 400-ml. beaker or a casserole are titrated with N/10 H_2SO_4, using two to five drops of methyl orange indicator (or 50 ml. can be similarly titrated with N/50 H_2SO_4).

To colored waters add 5 to 50 ml. H_2O_2 to decolorize. Start with 5 ml., and if this is insufficient, add more, 5 ml. at a time. This totally clears some waters; in all cases there is a great improvement. In correcting for the acidity of H_2O_2, our laboratory adds 0.1 ml. to the reading for each 5 ml. H_2O_2 used.

Calculate for 250-ml. sample.

No. ml. $\times 4 \times .005$ = g. per liter $CaCO_3$.
No. ml. $\times 4 \times 58.4 \times .005$ = grs. per gallon $CaCO_3$.
Or $\times 1.168$ = grs. per gallon $CaCO_3$.

Distilled water, and neutral waters containing magnesium chloride and magnesium sulfate frequently give an alkaline reaction when used with methyl orange. In such cases from .2 to .8 ml. N/10 acid are required to discharge the alkaline color of the methyl orange. Such a procedure would suggest to the operator that the waters were alkaline. However, if such neutral waters are boiled with phenolphthalein as an indicator for twenty minutes and no pink color develops, the waters are not alkaline but neutral. The use of a blank of .2 ml. is of no value under such conditions and it appears to the writer as much the safest way when the titration is under 1 ml. of N/10 acid that the water be boiled with phenolphthalein in an effort to determine absolutely whether this water is alkaline, due to the presence of a carbonate as indicated by the methyl orange, or whether the alkalinity is entirely due to the hydrolyzing of the calcium or magnesium base present in the absence of alkali. When no pink color is produced the water should be pronounced neutral.

Phenolphthalein may also be used as indicator on another 250-ml. portion, using the above procedure. This titration in connection with the methyl orange titration makes possible a determination of the relation of carbonate, bicarbonate and caustic alkalinity.

The following is adapted from a table on page 66, Standard Methods of Water Analysis of the American Public Health Association, and is of value in showing the relation of the various titrations. Methyl orange has been used in place of erythrosine.

TABLE SHOWING RELATION BETWEEN ALKALINITY BY PHENOLPHTHALEIN AND THAT BY METHYL ORANGE IN PRESENCE OF BICARBONATES, CARBONATES AND HYDRATES.

	Bicarbonates.	Carbonates.	Hydrates.
P = 0	M	0	0
P < $\frac{1}{2}$M	M–2P	2P	0
P = $\frac{1}{2}$M	0	2P	0
P > $\frac{1}{2}$M	0	2(M–P)	2P–M
P = M	0	0	M

M = Methyl orange alkalinity.
P = Phenolphthalein alkalinity.

PROPOSED METHOD OF TEST FOR THE DETERMINATION OF THE HYDROXIDE ION IN INDUSTRIAL WATER [12]

Scope.—There is no known method of chemical analysis by which the exact concentration of the hydroxide ion in water may be determined. Interpreta-

[12] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee D–19 on Water for Industrial Uses. This is a *proposed draft* and is published as information only. Comments are solicited and should be addressed to the Headquarters of the Society, 260 S. Broad St., Philadelphia, Pa.

tion of any titration method is complicated by the fact that when salts such as carbonate, phosphate, aluminate, silicate or chromate, as well as some types of organic material, are present, they are titrated to a greater or less extent along with the hydroxide ion. The standard method, employing strontium chloride, minimizes interference by sulfate, as well as by carbonate and phosphate. A method similar in procedure, but employing barium chloride, is outlined in the appendix following the standard method.

STANDARD METHOD [13]

This method is known as the strontium chloride method. It is based upon the fact that since strontium carbonate and strontium phosphate are much less soluble than strontium sulfate, it is possible to free the solution of carbonate and phosphate ions without precipitating sulfate. This procedure minimizes turbidity and permits the direct titration of the hydroxide ion.

Application.—This method is applicable in the examination of alkaline industrial waters such as boiler waters and boiler feedwaters under conditions where the water is practically free from organic matter, silicates and aluminates. If these ions are present in concentrations very low as compared with the concentration of the hydroxide ions the method may be used. It is not recommended where the concentration of these ions is high.

Solutions Required.—The following solutions will be required:

(*a*) ***Acid Solution.***—Hydrochloric or sulfuric acid, N/50, standardized, prepared from concentrated acid, reagent grade.

(*b*) ***Strontium Chloride Solution.***—4.5 g. $SrCl_2 \cdot 6H_2O$, reagent grade, per liter of distilled water.

(*c*) ***Phenolphthalein Indicator Solution.***—5 grams of phenolphthalein in 1 liter of 50% solution of ethyl alcohol.

(*d*) ***LaMotte Purple Indicator Solution.***—1% solution.

Procedure.—(*a*) 100.0 ml. of the sample containing not more than 150 p.p.m. of hydroxide ion shall be measured into a 250-ml. Erlenmeyer flask. If the concentration of hydroxide is known to be higher than 150 p.p.m., a correspondingly smaller sample shall be measured.

NOTE.—Thus, if the concentration of hydroxide were approximately 300 p.p.m., a 50-ml. sample should be measured.

[13] Edited from a method prepared by Subcommittee 8 of the Joint Research Committee on Boiler Feedwater Studies based on an investigation conducted under the direction of this Subcommittee which was described in the research publication of the American Society of Mechanical Engineers, "Determination of Carbonate, Phosphate and Hydroxide in Boiler Waters," published in September, 1933. The same general method, independently edited for use in the examination of stationary boiler waters, is included in the eighth edition of "Standard Methods for the Examination of Water and Sewage," published by the American Public Health Association.

(*b*) To this sample shall be added quickly 1.0 ml. of the strontium chloride solution for each 10 p.p.m. of carbonate ion present, 1.0 ml. for each 10 p.p.m. of orthophosphate ion present, and 4 ml. excess.

NOTE.—If the magnitude of phosphate and carbonate concentrations in the sample is not known it will be necessary to add sufficient strontium chloride solution to precipitate what is thought to be the maximum concentrations of these ions that could exist in the water. The excess strontium chloride will produce no interference but may increase the turbidity of the sample by precipitation of strontium sulfate.

(*c*) A stopper shall be placed at once very lightly in the flask. The flask shall then be heated to boiling with the stopper in place but not allowed to boil for more than two or three seconds. After standing hot for two or three minutes the flask shall be cooled, under water if desired. The stopper shall be in the flask at all times to prevent carbon dioxide from entering.

(*d*) If phosphate is *absent*, two or three drops of the phenolphthalein solution shall be added and the sample shall then be titrated with the N/50 acid until the phenolphthalein is colorless. The sample shall be swirled steadily during the addition of the acid to prevent redissolving of the precipitate.

If phosphate is *present*, two or three drops of the LaMotte Purple solution shall be added and the sample shall then be titrated to the endpoint of this indicator with the N/50 acid. A comparison blank should be used if the operator is not familiar with the endpoint of this indicator. The sample shall be swirled steadily during the titration.

NOTE.—The LaMotte Purple indicator is recommended when phosphates are present, since in this case the phenolphthalein endpoint at a pH value of 8 fades rapidly due to the resolution of strontium phosphate. At the LaMotte Purple endpoint above 9.3 this does not occur so readily. If LaMotte Purple solution of the concentration employed as a pH indicator is used in place of the 1% solution, 1 ml. is required.

Calculation.—The concentration of the hydroxide ion in terms of parts per million shall be calculated as follows:

$$OH^- = \frac{340}{S} \times f \times V$$

where S = the volume of the sample in ml.,
f = the acid correction factor,
V = the volume of acid in ml. used in the titration.

Accuracy.—When the concentration of hydroxide ion is greater than approximately 100 p.p.m. and the concentration of carbonate or of orthophosphate is not greater than 100 p.p.m. the values found should be accurate to within 2%. While the accuracy on a per cent basis will decrease with decrease in concentration of hydroxide ion or increase in concentration of carbonate or orthophosphate, the values found should be accurate to within a few parts per million unless other interfering substances such as chromates, aluminates, silicates, or some organic materials are present.

TOTAL CARBON DIOXIDE

The most accurate method for total carbon dioxide is that known as the evolution method which involves the decomposition of carbonates by an excess of acid, the carbon dioxide evolved being absorbed in a barium hydroxide solution of known acid equivalent. Titration of the remaining barium hydroxide with standard acid coupled with a separately determined pH value makes possible a calculation of carbonate and bicarbonate ions. This method is applicable where phosphates, silicates, chromates, and aluminates are present, but is affected by sulfides, sulfites, and other salts of volatile acids.

Evolution Method [14]

Apparatus.—A recommended form of apparatus is illustrated in Fig. 289. It consists of a box, open at the front, painted internally with a flat white paint and suitably illuminated. Upon this box three 50-ml. burettes are mounted non-rigidly by means of rubber stoppers fastened to the under side of the top. A small circulating pump sealed with mercury is connected as shown so that when two 500-ml. Erlenmeyer flasks are attached to the stoppers of burettes *B* and *C*, a closed system is established.

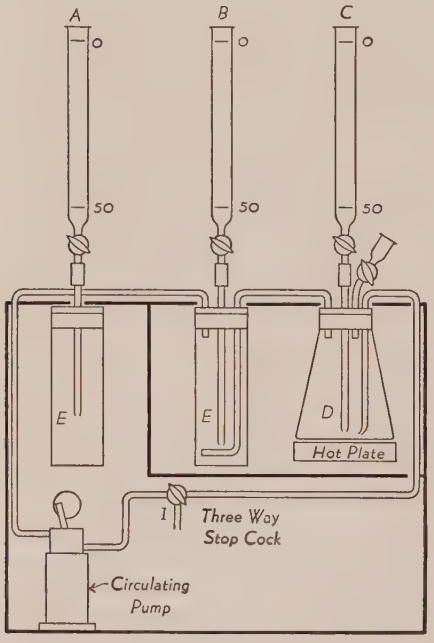


FIG. 289.—Evolution carbonate determination apparatus.

Solutions Required: ***Acid Solutions.***—(*A*) Sulfuric acid solution, N/10, standardized, prepared from concentrated H_2SO_4, reagent grade.

(*B*) Hydrochloric acid solution, N/50, standardized, prepared from concentrated HCl, reagent grade. 20 ml. of phenolphthalein solution shall be added to one liter of acid before it is standardized.

Barium hydroxide solution, N/50, prepared from $Ba(OH)_2 \cdot 8H_2O$, reagent grade. The acid equivalent of this solution shall be determined by using the evolution apparatus. A 50-ml. sample of barium hydroxide solution shall be measured from burette *A* into absorption flask *E*, which shall then be securely attached to the rubber stopper on burette *B*. Thereafter 200 ml. of distilled water free from carbon dioxide shall be placed in flask *D*, the pump started, and the gas circulated for about 10 minutes. The barium

[14] The Determination of Total Carbon Dioxide and of Carbonate and Bicarbonate Ions in Water. A. S. T. M. D–19, Subcomm. II.

hydroxide in flask *E* shall then be titrated with standard 0.02 N hydrochloric acid from burette *B* to the endpoint of phenolphthalein. The procedure outlined also serves to calibrate the apparatus against the air in the system.

Indicators.—(*A*) Phenolphthalein indicator solution. 5 g. of phenolphthalein dissolved in 1 liter of 50% ethyl alcohol. (*B*) Methyl orange indicator solution. 1 g. of methyl orange dissolved in 1 liter of distilled water.

Procedure: ***Manipulation.***—(*A*) 50 ml. of N/50 barium hydroxide solution shall be measured into flask *E* from burette *A*, and flask *E* shall then be securely attached to the rubber stopper on burette *B*.

(*B*) A 200-ml. sample of the water to be tested, containing not more than 100 p.p.m. of total carbon dioxide, shall then be placed in flask *D*, phenolphthalein indicator added, and the flask attached securely to the rubber stopper of burette *C*. The hot plate shall be put into position. The three-way cock shall then be opened to the atmosphere and the pump started. When bubbles appear in flask *D* the three-way cock shall be adjusted to circulate gas through the closed system comprising flasks *D* and *E*.

(*C*) With the gas circulating (to stir the solution), N/10 sulfuric acid shall be added from burette *C* to the sample in flask *D* until the phenolphthalein endpoint is reached. The amount of acid used shall be recorded.

(*D*) Two drops of methyl orange solution shall then be added to flask *D* and the titration continued to the methyl orange endpoint. The amount of acid used shall be recorded and then 20 ml. of acid added in excess.

(*E*) With the gas still circulating, the solution in flask *D* shall be heated until it just reaches the boiling point and maintained at this point for about 5 minutes. The hot plate shall then be turned off and the circulating pump stopped.

(*F*) The solution in flask *E* shall then be titrated with N/50 hydrochloric acid to the endpoint of phenolphthalein with constant swirling of the flask.

Calculation.—The results shall be calculated as follows:

(*A*) The concentration of total carbon dioxide in parts per million of CO_2 shall be calculated from the expression:

$$\text{total } CO_2 = (A - B) \times 2.2 \times f$$

where A = volume of 0.02 N acid equivalent to volume of N/50 $Ba(OH)_2$ used, in ml.,
B = volume of N/50 acid used, in ml.,
f = correction factor for N/50 acid.

(*B*) The concentrations of carbonate and bicarbonate ions in parts per million of CO_3 shall be estimated by means of the curves in Fig. 290. To use these curves, which express the respective fractions of the total carbon dioxide present as undissociated carbonic acid, as bicarbonate ion, and as carbonate ion, the pH of the original sample must be known. From the determined value of pH, the value of the fraction of the total carbon dioxide present as carbonate ion, as bicarbonate ion, and as undissociated carbonic acid, shall be read respectively from curves *a*, *b* and *c*, of Fig. 290. The concentrations of carbonate ion, bicarbonate ion, and undissociated carbonic acid in terms of parts per million, shall then be calculated from the expression

$$CO_3^{=} = (A - B) \times 3 \times f \times a$$
$$HCO_3 = (A - B) \times 3.05 \times f \times b$$
$$H_2CO_3 = (A - B) \times 3.1 \times f \times c$$

where a, b, and c are the fractions determined respectively from curves a, b, and c of Fig. 290 and the other symbols have the meaning defined above.

NOTE.—Since the preceding method of estimating ion concentrations is based upon data for the ionization of carbonic acid at 25° C., the values obtained hold for this temperature only. At any other temperature the ion concentrations will have the other values, which may be calculated if the dissociation constants of carbonic acid at this temperature are known.

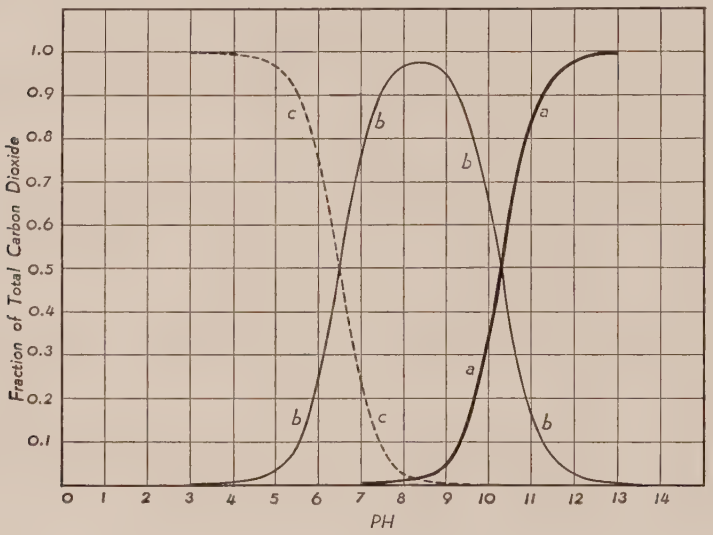


FIG. 290.—Fraction of Total Carbon Dioxide as pH.

Accuracy.—This method will yield results for total carbon dioxide accurate to 5% for concentrations as low as 10 p.p.m. of total CO_2.

Acidity

For acidity use N/10 Na_2CO_3 and 250 ml. water.

Acidity due to	Indicator.	Hot or Cold.
Carbonic and sulfuric acids, also Fe and Al sulfates	Phenolphthalein	Cold
Sulfuric acid, also Fe and Al sulfates	Phenolphthalein	Boiling
Sulfuric acid alone. When desired, 20 ml. N/10 H_2SO_4 may be added. Boil fifteen to twenty minutes, cool and titrate, noting the excess of acidity over the original 20 ml.	Methyl orange	Cold

Hydrogen-Ion Concentration

It is frequently desirable to know, particularly in connection with waters for certain industrial uses and the filtration of supplies using alum as a coagulant, the actual reaction of the water in terms of the hydrogen-ion concentration in addition to the familiar titration with methyl orange which gives the total available alkalinity of the water and does not indicate the actual dissociation or pH value. The proper adjustment of the pH value along with treatment using alum as a coagulant is necessary for economical and efficient operation of this process.[15] In the use of water for steam making and for certain manufacturing processes the added data given by this determination are making possible more accurate adjustments and more advantageous selection of supplies and treatments.

The most accurate method for making these measurements is by means of the hydrogen electrode;[16] however, colorimetric methods have proved satisfactory for use with water.[17] The following standard buffer solutions proposed by Clark and Lubs[18] together with their recommendations for the preparation and use of indicators make a convenient set of standards for this purpose, using 10 ml. of the standard buffer solution with five drops of the indicator compared with the sample used in the same proportions.

Indicator	pH Range	N/20 NaOH per Decigram
Methyl red	4.4–6.0	7.4
Brom thymol blue	6.0–7.4	3.2
Cresol red	7.2–8.8	5.3
Thymol blue	8.6–10.0	4.3

For the preparation of these solutions one decigram of the dry powder is ground in an agate mortar with the corresponding quantity of N/20 NaOH. When solution is complete, the thymol blue and brom thymol blue should be diluted to a 0.04% solution and the cresol red and methyl red to 0.02% solution.

The American Petroleum Institute[19] recommends the following set of standards.

Name	pH Range	Color Change
Brom phenol blue	3.0–4.6	Yellow–blue
Brom cresol green	4.0–5.6	Yellow–blue
Chlor phenol red	5.2–6.8	Yellow–red
Brom thymol blue	6.0–7.6	Yellow–blue
Phenol red	6.8–8.4	Yellow–red
Cresol red	7.2–8.8	Yellow–red

Solutions: ***M/5 Acid Potassium Phthalate.***—Make up a solution of potassium hydroxide dissolving about 60 grams of a high grade sample in about 400

[15] J. Ind. Eng. Chem., **14**, 395 (1922), 1038; Chem. Met. Eng., May 3, 1922, Vol. 26, No. 18; J. Am. W. W. Ass'n, Vol. 11, No. 3, May, 1924.

[16] Clark, The Determination of Hydrogen Ions (Williams and Wilkins, 1920).

[17] See also Index for additional discussion on colorimetric pH determination.

[18] Clark (see note 2).

[19] Code of Recommended Practice for the Treatment of Oil Field Waters. Report of Sub-Committee "C." Frank M. Beeson, Chairman. D. & P. E. Bull. No. 204, p. 8. American Petroleum Institute. Jan. 2, 1930.

ml. of water. To this add 50 grams of resublimed anhydrid of orthophthalic acid. Test a cool portion of the solution with phenolphthalein. If the solution is still alkaline, add more phthalic anhydrid; if acid, more KOH. When roughly adjusted to a slight pink with phenolphthalein, add as much more phthalic anhydrid as the solution contains and heat until all is dissolved. Filter hot and allow to crystallize slowly. Recrystallize at least twice from distilled water. Dry at 110°–115° C. to constant weight. A M/5 solution contains 40.828 grams per liter.

M/5 Potassium Chloride.—The salt should be crystallized three or four times and dried at 120° C. for two days. A M/5 solution contains 14.912 grams per liter.

M/5 Acid Potassium Phosphate.—Recrystallize three times from distilled water, dry at 110°–115° C. A M/5 solution contains 27.227 grams per liter.

M/5 Boric Acid, M/5 Potassium Chloride.—*M/5 Boric acid:* Recrystallize three times from distilled water, air dry in thin layers between filter paper and finally in a desiccator over $CaCl_2$ to constant weight. A M/5 solution contains 12.369 grams per liter of boric acid and 14.912 grams of potassium chloride.

M/5 Sodium Hydroxide.—Great care should be used in preparing this solution as free as possible from carbonate. It is preferable to use a factor rather than attempt exact adjustment. This solution should be kept in a paraffined bottle.

PHTHALATE—NaOH MIXTURES [20]

pH								
4.4	50 ml.	M/5 KH Phthalate	7.50 ml.	M/5 NaOH	Dilute to	200	ml.	
4.6	50 ml.	"	12.15 ml.	"	"	"	"	"
4.8	50 ml.	"	17.70 ml.	"	"	"	"	"
5.0	50 ml.	"	23.85 ml.	"	"	"	"	"
5.2	50 ml.	"	29.95 ml.	"	"	"	"	"
5.4	50 ml.	"	35.45 ml.	"	"	"	"	"
5.6	50 ml.	"	39.85 ml.	"	"	"	"	"
5.8	50 ml.	"	43.00 ml.	"	"	"	"	"
6.0	50 ml.	"	45.45 ml.	"	"	"	"	"

KH_2PO_4—NaOH MIXTURES

6.0	50 ml.	M/5 KH_2PO_4	5.70 ml.	M/5 NaOH	Dilute to	200	ml.	
6.2	50 ml.	"	8.60 ml.	"	"	"	"	"
6.4	50 ml.	"	12.60 ml.	"	"	"	"	"
6.6	50 ml.	"	17.80 ml.	"	"	"	"	"
6.8	50 ml.	"	23.65 ml.	"	"	"	"	"
7.0	50 ml.	"	29.63 ml.	"	"	"	"	"
7.2	50 ml.	"	35.00 ml.	"	"	"	"	"
7.4	50 ml.	"	39.50 ml.	"	"	"	"	"
7.6	50 ml.	"	42.80 ml.	"	"	"	"	"
7.8	50 ml.	"	45.20 ml.	"	"	"	"	"
8.0	50 ml.	"	46.80 ml.	"	"	"	"	"

BORIC ACID. KCl-NaOH MIXTURES

7.8	50 ml.	M/5 H_3BO_3, M/5 KCl	2.61 ml.	M/5 NaOH	Dilute to	200	ml.	
8.0	50 ml.	" "	3.97 ml.	"	"	"	"	"
8.2	50 ml.	" "	5.90 ml.	"	"	"	"	"
8.4	50 ml.	" "	8.50 ml.	"	"	"	"	"
8.6	50 ml.	" "	12.00 ml.	"	"	"	"	"

[20] Clark, The Determination of Hydrogen Ions (Williams and Wilkins, 1920).

8.8	50 ml.	M/5 H_3BO_3,	M/5 KCl	16.30 ml. M/5 NaOH	Dilute to 200 ml.
9.0	50 ml.	"	"	21.30 ml. "	" " " "
9.2	50 ml.	"	"	26.70 ml. "	" " " "
9.4	50 ml.	"	"	32.00 ml. "	" " " "
9.6	50 ml.	"	"	36.85 ml. "	" " " "
9.8	50 ml.	"	"	40.80 ml. "	" " " "
10.0	50 ml.	"	"	43.90 ml. "	" " " "

The standard buffer solutions prepared as described above may be used as permanent standards. The methyl red series often deteriorates within a short time, but if the series is checked at frequent intervals, any change may be corrected. Standards using indicators other than methyl red have been used for four weeks before any change in color could be detected. In order to prevent the growth of mold, one drop of toluol may be added to each tube before sealing. If the tubes are corked, paraffined stoppers should be used and for accurate comparison tubes of equal diameter should be chosen.

Free Carbonic Acid [21]

Reagents.—Either standard N/10 sodium carbonate or standard N/22 sodium carbonate. For the latter dissolve 2.41 grams of dry sodium carbonate in one liter of distilled water which has been boiled and cooled in a carbon dioxide free atmosphere. Hold both solutions in glass bottles protected by tubes filled with soda-lime.

One ml. N/10 $Na_2CO_3 = 2.2$ milligrams CO_2.
One ml. N/22 $Na_2CO_3 = 1.0$ milligram CO_2.

Operation.—With N/10 sodium carbonate titrate 250 ml. of sample in 400-ml. beaker, using phenolphthalein as indicator. First faint but permanent pink denotes endpoint.

Using 250 ml.

No. ml. N/10 $Na_2CO_3 \times 8.8 = CO_2$ parts per million.
No. ml. N/10 $Na_2CO_3 \times .513 = CO_2$ grains per gallon.

With N/22 sodium carbonate solution, use 100 ml. of sample, preferably in 100-ml. Nessler tube, titrate and rotate the tube until faint but permanent pink color 30 seconds without fading is produced, using phenolphthalein as indicator.

Using 100 ml.

No. ml. N/22 $Na_2CO_3 \times 10 = CO_2$ parts per million.
No. ml. N/22 $Na_2CO_3 \times .583 = CO_2$ grains per gallon.

Chlorine

Titrate 100 ml. of water, using 1 ml. of 10% potassium chromate as an indicator, with N/10 $AgNO_3$ to first permanent indication of the red silver chromate. (Acid waters should be neutralized and sulfide waters boiled with a drop or so of nitric acid and then neutralized for reliable results.)

[21] For criticisms of this method see Z. Nahr. Genussm., **24**, 429 (1912); also C. A., **7**, 38 (1913).

No. ml. $\times 3.42$ = grs. per gallon NaCl.
No. ml. $\times 58.46$ = parts per million NaCl.
No. ml. $\times 35.46$ = parts per million Cl.

NOTE.—Where qualitative test shows chlorine to be high, smaller portions of the sample should be taken, either by certified pipette, or burette, and when the titration with N/10 $AgNO_3$ is less than .2 ml., N/50 or N/100 $AgNO_3$ should be used for accuracy.

Nitrates

(Also see Sanitary Analysis)

PHENOLSULFONIC ACID METHOD

Reagent: 1. ***Phenolsulfonic Acid.***—Dissolve 25 grams of pure white phenol in 150 ml. of pure concentrated sulfuric acid, add 75 ml. of fuming sulfuric acid (15% SO_3), stir well and heat for two hours at about 100°.[22]

2. ***Ammonium hydroxide*** 1:1.

3. ***Sodium Carbonate.***—10% solution of anhydrous Na_2CO_3.

4. ***Standard Nitrate Solution.***—Dissolve 0.72 gram pure or c.p. potassium nitrate in 1 liter of distilled water. Evaporate carefully 10 ml. of this solution on water bath, moisten thoroughly with 2 ml. of solution No. 1 and dilute to 1 liter. 1 ml. of this = 0.001 milligram of nitrogen.

Determination.—Carefully evaporate 100 ml. of water after the addition of 2 ml. of sodium carbonate solution. After this evaporate to dryness, cool and add 2 ml. phenolsulfonic acid (No. 1), mixing well with a glass rod. Dilute with 25 ml. of distilled water and add an excess of ammonium hydroxide, making up to 100 ml. volume with distilled water.

The dilute solution is then compared with the standard solution.

NOTES.—When the chlorides are over 100 parts per million in the original sample they should be removed with the addition of silver sulfate in the solid form and the water should be filtered prior to evaporation. It is for this reason that ammonium hydroxide is used to develop the color instead of potassium hydroxide, which is frequently recommended, as a slight excess of silver sulfate will result in a dirty precipitate when using potassium hydroxide, whereas the use of ammonia has no effect. Furthermore, the filtration of a turbid nitrate solution does not result in a satisfactory color, as would be the case without filtration.

Permanent standards can be made by procedure given on page 2053, or standards can be made using tripotassium nitrophenoldisulfonate. The following method is given in an article in J. Am. Chem. Soc., **33**, 381 (1911).

The theoretical amount of powdered potassium nitrate is added to the disulfonic acid reagent in small pinches at a time (for each ml. of reagent 0.1076 gram KNO_3), stirring thoroughly after each addition. The product is then diluted, treated with dry barium carbonate to a deep yellow color, filtered and the precipitate washed with boiling water to remove the barium salt which is but slightly soluble in cold water. This extraction must be thorough. Filtrates and washings are united, the barium removed by the addition of potassium carbonate until alkaline, the solution filtered and the filtrate concentrated and crystallized. The solution may then be easily purified by crystallization. In preparing the standards, however, solutions made from known amounts of nitrate standards will match up with this recrystallized solution, and by means of proper dilutions the series of standards can be made. Standards made this way will last for many months, whereas standards made from the standard nitrate solution are apt to lose value in a month's period and should be made up very frequently.

[22] J. Am. Chem. Soc., **33**, 382, 1911.

Where nitrates are high, 85 to 90 parts per million, or 5 grains per gallon and over, colorimetric methods do not always give reliable results, and 500 ml. of the water should be first boiled with a slight excess of acid, then made alkaline with sodium or potassium hydroxide, reduced with 10 grams each of powdered Zn and Fe, or 10 grams powdered Al, and distilled into an excess of N/10 or N/100 HCl, as the case may be, and titrated back, using cochineal as indicator, and calculating the ammonia absorbed to NO_3 or $Ca(NO_3)_2$ as desired. (Where free ammonia or its compounds are present corrections must be made.)

A recent modification of this method depends upon the absorption of ammonia into a solution of boric acid (5 grams boric acid in 100 ml. of water). Due to the very weak acidity of the boric acid, it is possible to titrate the ammonia direct with standard acid, using methyl orange as an indicator, and this has the advantage of doing away with two standard solutions. The boric acid strength is based upon 5 grams of boric acid to 100 ml. of water to each .2 gram of ammonia absorbed. It is stated that even the cooled condenser is unnecessary in this absorption.[23]

Ammonia and Its Compounds

Place 500 ml. or less in an 800-ml. Kjeldahl flask, make alkaline and distill into N/10, or weaker, HCl, titrate with cochineal or Nesslerize. (See Sanitary Analysis, page 2049.)

Total Mineral Residue

Use a clean weighed platinum dish. Evaporate 50 ml. (certified pipette) to dryness at about 130° C. and bake for at least thirty minutes at that temperature. Ordinary water-bath temperature will not remove water of crystallization from Na_2SO_4 or $CaSO_4$. Weigh to the fourth decimal or .0001 gram.

$$\text{Weight} \times 1168 = \text{grains per gallon.}$$
$$0.1 \text{ milligram} = 2 \text{ parts per million.}$$

Residues of acid waters should be ignited to a dull red heat. Where the acidity is low a drop or so of sulfuric acid should be added to assure the fixation of all sodium and potassium salts as the sulfate. The ignition should be complete so that no free acid is left behind and to assure the decomposition of all iron compounds to the oxide form. In calculating, correction must be made for the change in the iron salts and all other compounds converted to the sulfate form for comparison with the sulfated residue, and then the proper corrections made to give the theoretical residue on the original water.

Residues with much organic matter, after weighing, may be gently ignited until the carbon has been burned off, cooled, recarbonated with tested $(NH_4)_2CO_3$, dried and again weighed. The difference in weight after titrating for possible volatilized chlorides gives approximately the organic matter present.

[23] The Volumetric Determination of Ammonia. L. W. Winkler, Budapest. Z. angew. Chem., **26**, I, 231 (1913).

Determination of Ammonia by the Boric Acid Method. L. W. Winkler, Z. angew. Chem., **27**, I, 630–2 (1914).

The Determination of Ammonia by the Boric Acid Method. E. Bernard, Z. angew. Chem., **27**, I, 664 (1914).

Waters high in easily decomposed $MgCl_2$ or $Ca(NO_3)_2$ should be evaporated with a few drops excess of H_2SO_4, or Na_2CO_3, and the residue compared with an addition of all bases calculated to the sulfate form, or corrected for added carbonate.

NOTE.—When acid is used, ignite to a dull red heat; when carbonate, evaporate as in the case of the original residue.

Hydrogen Sulfide

Due to the fact that hydrogen sulfide is frequently very transient and often oxidizes to sulfate in transit, it is advisable to collect this sample in a special container at the point of sampling. Two or three bottles holding exactly 250 ml. of water each, are used, each bottle containing 50 ml. N/100 iodine solution. After filling, the bottle is sealed. The sample is titrated with standard N/100 sodium thiosulfate upon receipt at laboratory, at which time a blank is run, using 50 ml. iodine solution made to mark with distilled water. The difference between the titration of the sample and the blank represents hydrogen sulfide present.

Iodine value $\times 0.1263 \times 4 =$ sulfur value grams per liter.

When hydrogen sulfide is determined on samples already collected and submitted, 100 ml. of the sample is oxidized with bromine (about 10 ml. is sufficient), HCl is also added, and it is then boiled until colorless, after which sulfates are precipitated with $BaCl_2$ as already described. The difference between the oxidized and unoxidized sulfates is calculated to H_2S.

Oil

Frequently waters from condensing engine, or after passing heaters or oil separators, still contain oil in small quantities. The following method has been found most satisfactory:

Reagents: ***Ferric Chloride Solution.***—(10 grams of iron dissolved in 200 ml. HCl, oxidized with HNO_3 and made to one liter.)

Ammonia c.p.

Operation.—Add to the water taken in a large beaker or flask 5 ml. of the "ferric chloride" solution and heat nearly to boiling; then add ammonia in excess, to precipitate the iron (which precipitate contains all the oil), and boil for two minutes.

NOTE.—If the oil exceeds 0.4 grain per gallon, use 500 ml., or less for the determination; if below 0.4 grain per gallon use 1 liter.

Allow to stand a few minutes and filter through a 15 cm. filter paper which has been previously extracted with ether, transferring the precipitate onto the paper with hot water, and washing three or four times with hot water. Then dry both filter and precipitate in the water oven at 100° C. and when dry, extract with ether in the Soxhlet in the usual way, evaporate the ether extract and weigh the remaining oil.

Optional Method for Oil.—Shake up the sample of water in a separatory funnel with 25 ml. ethyl ether or 25 ml. of benzol and separate the extract con-

taining the oil. Three extractions, as directed above, will remove all oil from the water. The solvent is expelled by warming gently and the oil is weighed.

Dissolved Oxygen

Use the Winkler Method [24]

Reagents: No. 1. *Manganous Sulfate Solution.*—48 grams manganous sulfate dissolved in 100 ml. distilled water.

No. 2. *Iodide Solution.*—360 grams NaOH and 100 grams KI dissolved in 1 liter of distilled water

No. 3. *Concentrated hydrochloric acid, or sulfuric acid sp.gr. 1.4 (dilute 1 : 1).*

No. 4. *Sodium Thiosulfate Solution.*—N/100 solution is made as needed from the N/10 stock solution.

Note.—Not permanent; should be frequently restandardized against N/100 potassium bichromate.

The addition of 5 ml. of chloroform plus 1.5 grams sodium or ammonium carbonate to each liter of solution on mixing will improve its keeping quality.

N/40 sodium thiosulfate containing 6.2 grams C.P. recrystallized salt per liter may be preferred to N/100 strength. 1 ml. of this solution is equivalent to 0.2 milligram oxygen by weight or 0.1395 ml. oxygen by volume, standard conditions.

5. *Starch Solution.*[25]—The starch should first be made into a thin paste with cold water and about 200 times its weight of boiling water stirred in and boiled for a few minutes. A few drops of chloroform will assist in preserving this solution.

Collection of Sample.—A small-necked, 250-ml. bottle should be used, etched or otherwise marked, with its exact volume previously determined. The collection should be so arranged to exclude outside air and result in several continuous changes of the contents before stoppering, care being taken to exclude air bubbles.

Operation.—To sample as received add, in both cases by pipette, delivering below surface of water and away from the air, 2 ml. solution No. 1 (manganese sulfate) and No. 2 (NaOH, KI). Restopper and shake thoroughly. After precipitate has settled add 2 ml. HCl or H_2SO_4 and again mix by thorough shaking until precipitate has completely dissolved, transfer 100-ml. to flask, and titrate with solution No. 4 (sodium thiosulfate), using starch as indicator near end as the color approaches a faint yellow.

N = ml. N/100 thiosulfate solution.
V = capacity of bottle less 4 ml. (vol. sol. 1 and 2 added).
O = the amount of oxygen in parts per million in water saturated at the same temperature and pressure.

[24] Ber., **21**, 2843 (1888). Also Z. Anal. Chem., **53**, 665–72 (1914); C.F.C.A., **8**, 674 (1915).

[25] Hale gives the following method. "Rub 5 grams of potato starch with cold water to a thin paste together with 10 milligrams of mercuric iodide. Pour into one liter of boiling water and boil half an hour."

(1) Oxygen in p.p.m. $= \frac{0.0008N \times 1{,}000{,}000}{100} = .8N$.[26]

(2) Oxygen in ml. per liter = .7 oxygen p.p.m.

(3) Oxygen per cent saturation $= \frac{\text{Oxygen p.p.m. (observed temp. and pres.)} \times 100}{\text{Saturation oxygen p.p.m. (observed temp. and pres.)}}$.

METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF LEAD, ZINC, COPPER AND TIN

Very frequently a determination is desired of materials which are apt to be present in water due to the solvent action of such water upon pipes and containers. In most cases the estimates are made by colorimetric methods if the amounts present are exceedingly small. As these determinations are made only in rare cases it seems advisable to summarize, calling attention to the fact that all methods may be found in full in any of the editions of Standard Methods for Water Analysis gotten out by the American Public Health Association.

Where any or all of the metals, lead, zinc, copper and iron are apt to be present, a large quantity (1 to 4 liters), of the water is evaporated. The metals are separated as sulfides with ammonia and hydrogen sulfide. The precipitate after washing is dissolved in nitric acid and refiltered to remove suspended matter and then concentrated with H_2SO_4.

The lead is removed by taking up the concentrated solution with 50% alcohol (100 ml. to 150 ml.), filtering and dissolving the precipitate in ammonium acetate, after which the solution is made to volume and divided. One-half is saturated with hydrogen sulfide water to get an approximate idea of the amount of lead present. To the other half add two to three drops of acetic acid, then an excess of hydrogen sulfide water and compare the color with standards. This gives ***lead.***

The alcohol is removed from the filtrate by evaporation and it is then treated with ammonia to remove possible iron. The filtrate from the iron precipitate is neutralized with H_2SO_4, then 2 ml. concentrated H_2SO_4 and 1 gram urea added. Copper is removed by electrolyzing (two hours with 0.5 ampere current). If the deposit is material it may be weighed as copper after washing with alcohol and drying. When the deposit is extremely small it should be dissolved in nitric acid, evaporated to dryness to remove acid taken up in water, after which potassium sulfide solution is added and the color compared with standards. This gives ***copper.***

[26] Correcting for displacement for 300-ml. bottle, .8N = .811N; for 275-ml. bottle, .8N = .812N.

No correction for displacement affects result .1 p.p.m. oxygen.

Twenty-five ml. variation in capacity of bottle affects result .01 p.p.m. oxygen.

The above formulæ are based upon N/100 thiosulfate, and titrating 100 ml. volume. N = milliliters thiosulfate used.

The solution from the above is nearly neutralized with ammonia. It is then concentrated and 2 grams potassium oxalate and 1.5 grams potassium sulfate are added and the zinc removed by electrolyzing. (Three hours with 0.3 ampere current.) This gives *zinc.*

Where copper only is desired it is frequently sufficiently satisfactory to concentrate the water from 50 ml. to 75 ml., after which it is acidified with 2 to 5 ml. concentrated H_2SO_4, depending upon whether the water is very alkaline with carbonate of lime, etc., and then the procedure for copper is followed.[27]

There is no satisfactory method for the quantitative determination of small quantities of tin. In the above-mentioned procedure, however, in case tin should be present it would be removed with the ammonia precipitate for the removal of iron and its presence may be avoided by dissolving the sulfides in the original precipitation in HNO_3, in which the tin would remain behind insoluble.

HARDNESS

Total Hardness

The most accurate method for total hardness is by calculation of the calcium and magnesium determined gravimetrically as previously outlined, calculating the calcium as calcium carbonate and the magnesium to its calcium carbonate equivalent in terms of parts per million.[28] However, where only the hardness is desired, gravimetric methods are cumbersome and the following are accepted as standard.

The standard method for the determination of total hardness, as well as temporary and permanent, depends upon the action of the lime and magnesia in solution upon soap, the soap added in a very dilute solution in alcohol. Total hardness represents the total soap acted upon by the water in its original state, permanent hardness represents the total soap acted upon by the water after the water in question has been thoroughly boiled and separated from the suspended matter, and temporary hardness represents the difference between the total hardness and the permanent hardness, and while it is supposed to represent combined carbonates of lime and magnesia, and the permanent hardness is supposed to represent lime and magnesia in other forms than carbonate, this is rarely so due to the fact that a certain material amount of carbonate of lime and magnesia is soluble in water, even in the absence of carbon dioxide gas.

The hardness [29] is considered entirely due to Ca, when the amount of soap used is calculated. The errors due to Mg and Fe present are not considered; as a rule the blank on distilled water equivalent to the amount of sample is not considered.

Preparation of Solutions: The reagents used are *standard soap solution* and

[27] Phelps, J. Amer. Chem. Soc., **28**, 369 (1906).
[28] C. Bahlmann, J. Ind. Eng. Chem., **6**, 209, 11 (1914).
[29] Errors in the Clark Method for Determining Hardness, George G. Town, J. Am. Water Works Assoc., **21**, 1395 (1929).

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standard calcium chloride solution, the latter being made under such conditions that 1 ml. of the solution is equivalent to 0.2 milligram of calcium carbonate.

Standard Calcium Chloride Solution.—0.2 gram pure calcium carbonate is dissolved in a small amount of dilute HCl, taking pains to avoid any loss due to effervescence or spattering. Evaporate the solution to dryness several times to remove excess acid. Dissolve in distilled water and make up to 1 liter.

Standard Soap Solution is obtained by dissolving approximately 100 grams dry Castile soap in 1 liter 80% alcohol. This solution should stand several days. For standardizing this solution should be diluted with alcohol (70% to 80%), until 6.4 ml. when added to 20 ml. of standard calcium solution will produce a permanent lather. Usually less than 100 ml. of the original soap solution will make 1 liter of standard solution.

For plant control, and to simplify calculations, 58.3 ml. is frequently the quantity taken, and the soap solution standardized so that 4.5 ml. = 20 ml. standard $CaCl_2$; a correction by subtracting 0.5 from all readings is made, and in the resulting figure 1 ml. will be equivalent to 1 mg. $CaCO_3$. If the standard soap solution is used and the figures to read in grains per gallon are desired, take 41 ml. of sample and subtract a correction of 0.7 ml. from the reading obtained.

For standardizing, use 250-ml. glass-stoppered bottle, add 20 ml. calcium solution with 30 ml. distilled water. The soap solution should be added from a burette, approximately .2 ml. at a time, after which the bottle is shaken vigorously until the lather formed remains unbroken for five minutes after shaking and after the bottle has been placed upon its side.

NOTE.—Pure potassium oleate may be used in place of soap.[30]

Operation.—Fifty ml. of the water in question are measured into a 250-ml. bottle, the soap solution added, approximately .2 ml. at a time, and in the same manner as described for the standardizing of said soap solution. The following table, copied from p. 33, Standard Methods of Water Analysis, A. P. H. A., 1913, may be used to obtain the total hardness from the results so noted:

TABLE OF HARDNESS SHOWING THE PARTS PER MILLION OF CALCIUM CARBONATE ($CaCO_3$) FOR EACH TENTH OF A MILLILITER OF SOAP SOLUTION WHEN 50 ML. OF THE SAMPLE ARE USED.

ml. of Soap Solution.	0.0 ml.	0.1 ml.	0.2 ml.	0.3 ml.	0.4 ml.	0.5 ml.	0.6 ml.	0.7 ml.	0.8 ml.	0.9 ml.
0.0	....	....	....	....	....	....	....	0.0	0.6	3.2
1.0	4.8	6.3	7.9	9.5	11.1	12.7	14.3	15.6	16.9	18.2
2.0	19.5	20.8	22.1	23.4	24.7	26.0	27.3	28.6	29.9	31.2
3.0	32.5	33.8	35.1	36.4	37.7	38.0	40.3	41.6	42.9	44.3
4.0	45.7	47.1	48.6	50.0	51.4	52.9	54.3	55.7	57.1	58.6
5.0	60.0	61.4	62.9	64.3	65.7	67.1	68.6	70.0	71.4	72.9
6.0	74.3	75.7	77.1	78.6	80.0	81.4	82.9	84.3	85.7	87.1
7.0	88.6	90.0	91.4	92.9	94.3	95.7	97.1	98.6	100.0	101.5

[30] C. Blacher, Chem. Ztg., **36**, 541 (1912); J. Soc. Chem. Ind., **31**, 555 (1912); C.A., **7**, 1394 (1913); C. Blacher, P. Gruenberg, M. Kissa, Chem. Ztg., **37**, 56–8 (1913); C.A., **7**, 1938 (1913). L. W. Winkler, Z. Anal. Chem., **53**, 409–15 (1914); C.A., **8**, 2912 (1914).

It is not desirable to use more than 7 ml. of soap solution for 50 ml. of the water, and when the figures are higher, the water should be diluted with distilled water. The reading in the table corresponding to the ml. of soap solution used is then multiplied by the quotient $\frac{50 \text{ ml.}}{x \text{ ml.}}$; x ml. being equal to the amount of water taken. In making this determination there is frequently noted a false end-point sometimes known as the magnesium end-point. To avoid error, it is advisable, after completing the titration, to read the burette, add 0.5 ml. more of the soap solution and shake well. If magnesium has been responsible for the false end-point, after such addition the later will again disappear, and titration should be continued until a new and true end-point is reached. It is advisable to determine the strength of the soap solution from time to time, as it is very prone to change upon standing. Results should be recorded in terms of calcium carbonate, parts per million. There are various other means of reporting. The English degree frequently noted as Clark degree, represents grains calcium carbonate per Imperial gallon and should be multiplied by 14.3 to give parts per million. Conversely, the result obtained in parts per million divided by 14.3 will give Clark, or English degrees. French degrees represent parts per 100,000 calcium carbonate and should be multiplied by 10 to give parts per million. Conversely, division of the result obtained above by 10 will give French degrees. German degrees represent parts per 100,000 calcium oxide and should be multiplied by 17.8 to give parts per million calcium carbonate. The determination of hardness is not reliable on account of the varying action of calcium and magnesium salts, and should never be resorted to when possible to determine these bases direct.

Note.—Dr. Hale claims that the soap method for hardness in skilled hands is accurate from 10 to 15 parts per million on waters as hard as 300 parts.

For *permanent hardness* the standard soap solution is used as above stated. The water, however, is boiled gently for one-half hour, allowed to cool, made to volume with boiled and cooled distilled water and filtered, after which the above method is used. The difference between total hardness and permanent hardness is supposed to represent temporary hardness. The *alkalinity* determination given on a previous page is a much more accurate method of determining temporary hardness, however, and is also much more easily carried out. When total hardness and alkalinity are determined, permanent hardness would be the difference between these two figures. For comparative use as against ***total*** and ***permanent*** hardness determined as such, the results would be much different, as the alkalinity determination of all the carbonates would give a permanent hardness representing absolutely non-carbonate hardness; whereas the determined permanent hardness would contain a material amount of combined carbonates of lime and magnesia. The American Public Health Association, Committee on Standard Method of Water Analysis, recommend that the determination of permanent hardness by the soap solution be discontinued in connection with softening process, as it is so unsatisfactory in general practice.

Magnesium Chloride

Frequently, when hypothetical combinations are used it is desired to check up these calculated combinations by some chemical method. Magnesium

chloride is frequently produced in the course of hypothetical combinations and its presence is as frequently a source of much trouble in the determination of a mineral residue, owing to the ease with which it decomposes or carbonates. A method is suggested whereby a second 50 ml. portion similar to the total mineral residue is exactly neutralized with sufficient H_2SO_4, the amount to use being calculated from the total alkalinity obtained elsewhere. The solution is allowed to go to complete dryness, is baked at a temperature of 280° F. to 300° F., and after being cooled the chlorine is titrated. The difference between the chlorine thus determined and the total chlorine previously determined represents chlorine lost by volatilization as magnesium chloride. In the absence of organic matter this method is approximately accurate. Where organic matter or other reducing material is present, however, the results are not so satisfactory.

Calcium Sulfate

In a similar manner it is frequently desired to know whether or not a water would contain calcium sulfate, and a method of comparative satisfaction depends upon the evaporation of 250 ml. to 500 ml. of the original water to dryness. After cooling, 10 ml. of distilled water are added and the mineral matter loosened from the sides of the dish and partially dissolved. Ten ml. of 95% alcohol are then added and 100 ml. of 50% alcohol. After thorough stirring and solution this material is filtered, the precipitate washed with 50% alcohol and the filtrate made to volume, divided and tested for calcium and sulfates in the usual manner. The method is only approximate.

LIME AND SODA VALUE [31]

Two very simple methods have been devised for the rapid estimation of the amount of lime and soda-ash necessary for softening, when water treatment is considered from the outside softening-plant point of view.

Value for Lime

Reagents: ***Saturated lime water*** (strength to be known for each series of determinations). ***N/10 hydrochloric acid.***

Process.—Take 200 ml. of the water in question; add 50 ml. saturated lime-water solution in 250-ml. volumetric flask and heat to boiling. Allow to cool. Fill to the 250-ml. mark with water to replace that lost by evaporation; filter through a dry-folded filter and titrate 200 ml. of the filtrate with N/10 acid, using methyl orange as an indicator.

For calculation, let *a* equal number of ml. N/10 calcium oxide in 50 ml. the lime water, as determined: and let *b* equal the number ml. N/10 hydrochloric acid used in determination.

[31] Drawe, Zeit. angew. Chem., **23**, 52 (1910).

$(4a-5b)\times 3.51$ CaO will give milligrams of lime per liter required to soften the water tested.

Value for Soda

To the neutralized 200 ml. from above titration, add 20 ml. N/10 sodium carbonate. Heat to boiling. Transfer with CO_2 free distilled water into a 250-ml. flask to make up to mark with washings from the dish; mix thoroughly and filter, collecting 200 ml. of the filtrate in a beaker. Titrate with N/10 hydrochloric acid for the excess alkali. Designate the number of ml. in this titration by *c*.

Formula: $(20-b-\frac{5}{4}c)\times 33.13$ Na_2CO_3 = milligrams of soda per liter necessary to soften water in question.

NOTE.—Both formulæ are based upon C. P. chemicals, and corrections must be made for the value of the commercial materials in use. These methods are valuable, though for actual practice it is advisable to try out on a liter of water in question, using the calculated amounts of lime and soda for experimental purposes.

METHODS OF REPORTING AND INTERPRETATION

The manner of reporting the results of a mineral analysis of any water calls for as much thought and uniformity as the methods of analysis themselves, and in this department there is much less uniformity than in the case of analytical methods. Undoubtedly, the ideal method of reporting is that which gives results in ionic form (positive and negative radicals), in terms of parts per million or grains per gallon. The latter term is purely American and would have to be converted for comparison with results obtained in almost any foreign country. Parts per million, though newer and still unfamiliar to all but professional and scientific men, is gaining gradually a strong foothold, and the consideration of this terminology with the ionic form of reporting will be considered prior to the discussion of hypothetical combination and grains per gallon.

Mr. Herman Stabler,[32] and R. B. Dole,[33] of the United States Geological Survey, have devised and simplified certain calculations and formulas, which greatly assist in the interpretation, comparison, and classification of waters for Industrial and Irrigation [34] purposes. Formulas with reference to dissolved solids will be the only ones discussed here. The following table gives reaction coefficients:

[32] Eng. News, **60**, 355 (1909).
[33] Water Supply Paper No. 274, p. 165, Water Supply Paper No. 254, J. Ind. Eng. Chem., **6**, 710 (1914).
[34] U. S. G. S. W. S. Paper, 274, p. 177.

Positive Radicals.	Reaction Coefficients.	Negative Radicals.	Reaction Coefficients.
Ferrous Iron (Fe)	0.0358	Carbonate (CO_3)	0.0333
Aluminum (Al)	.1107	Bicarbonate (HCO_3)	.0164
Calcium (Ca)	.0499	Sulfate (SO_4)	.0208
Magnesium (Mg)	.0822	Chlorine (Cl)	.0282
Sodium (Na)	.0435	Nitrate (NO_3)	.0161
Potassium (K)	.0256		
Hydrogen (H)	.992		

Using the above table, the parts per million of each radical multiplied by its reacting coefficient will give its reacting value, and in the formulas which follow this will be indicated by r prefixed to the chemical symbol of the radical.

For checking the accuracy of the analysis, the sum of the positive reacting values should equal the sum of the negative reacting values, and the formula, $100\frac{r\text{ Pos.}-r\text{ Neg.}}{r\text{ Pos.}+r\text{ Neg.}}=E$, the percentage error of the analysis. The value of this error should never exceed 5 for waters of 100 p.p.m. or more dissolved solids, and should be 2 or less.

In ordinary analysis, silica, iron and aluminum are present in such small quantities that they may, for simplicity's sake, be ignored. The following formulas are given without comment, as full details can be found in Water Supply Paper No. 274.

Water Softening

For 1000 Gals. Water.—Pounds lime (90% CaO) required
$$=0.26(r\text{Fe}+r\text{Al}+r\text{Mg}+r\text{H}+r\text{HCO}_3+.0454\ \text{CO}_2).$$

Pounds soda ash (95% Na_2CO_3) required
$$=0.465(r\text{Fe}+r\text{Al}+r\text{Ca}+r\text{Mg}+r\text{H}-r\text{CO}_3-r\text{HCO}_3).$$

Note.—Dr. Hale states the following. "Instead of the extended formulæ of the ionic system, I much prefer my simple formulae.

(Alkalinity $\times .44$ + free CO_2) $\times .0106$ = lbs. CaO per 1000 gals. feed water.
Also (Total hardness − total lime) $\times .0047$ = lbs. CaO per 1000 gals. feed water. or total magnesia as $CaCO_3$.
(Total hardness − alkalinity) $\times .009$ = lbs. Na_2CO_3 per 1000 gals. feed water. Expressed as $CaCO_3$."

Foaming and Priming

Foaming coefficient F = 2.7 Na.

Taking into consideration the various boilers and the action of various waters in practice, the following approximate classification of waters for foaming conditions is of value:

Non-foaming, F = 60 or less.
Semi-foaming, F = 60–200.
Foaming, F = 200 or more.

Corrosion

For Acid Waters

Coefficient of corrosion $C = 1.008(rH + rAl + rFe + rMg - rCO_3 - rHCO_3)$.

For Alkaline Waters

$C = rMg - rHCO_3$.

If C is positive, water will corrode.

If C+.0503 Ca is negative, water will not corrode on account of the mineral materials in the water.

If C is negative, but C+.0503 Ca is positive, the water may or may not corrode.

Scale

$SiO_2 + 2.95\ Ca + 1.66\ Mg = \text{scale p.p.m.},$

or

[35] (.00833 Sm+.00833 Cm+.3 *r*Fe+.142 *r*Al)+.168 *r*Mg+.492 *r*Ca = scale lbs. per 1000 gallons.

There are also formulas given in the above-mentioned Bulletin on soap cost, lime, soda, soda ash, cost hard scale (pounds per 1000 gallons) and a hardness coefficient of the scale formation.

Hypothetical Combinations

The use of hypothetical combinations in the reporting of a mineral water is frequently of value, in that it gives a more rapid way of placing in simpler terms the principal materials present in the water. It should never be assumed from the hypothetical combinations that the materials so reported are present in the water in that particular form, but it is assumed by most, that the form in which such materials are reported will represent the condition in which those materials will combine when the water is subjected to increased pressure and increased temperature. In other words, the hypothetical combinations most generally in use represent the way materials will appear when combined, due to the law of mass action under steam-boiler conditions.

For such purpose the method which takes care of the insoluble materials or materials leaving the water first is the most common method in use. This method combines as follows: Where the sum of the sulfate and carbonate radicals exceeds that of lime and magnesia as bases, the magnesia is first calculated to carbonate, the remaining carbonate is combined with lime, the remaining lime with sulfate and the remaining sulfate with sodium. This also takes care of the general condition where the carbonates alone are in excess of the combined carbonates of lime and magnesium, in which case the remaining carbonate naturally would be calculated to sodium and all the sulfate, as well as chloride, also, calculated to sodium. Where, however, the sum of the bases is greater than the sum of the carbonate and the sulfate radicals, two possible conditions

[35] Can be omitted or ignored unless suspended matter, silica, etc., are present in large quantities.

or combinations exist. Where magnesium chloride is present in the water, the sum of the acids calculated to the soda radical should be greater than the total mineral residue. Partially decomposed magnesium chloride is indicated in this way, also the fact that magnesium chloride has a lower molecular weight than sodium chloride, which condition would be indicated in such a comparison. When this case exists, the sulfate is first calculated to calcium, the remaining calcium to carbonate, the remaining carbonate to magnesium, the remaining magnesium to chloride, the remaining chloride to sodium. Where the total mineral residue is greater than the sum of the acids and where nitrates are present, we then have nitrate of lime, which is assumed to be present rather than magnesium nitrate, and the calculations are as follows: All the sulfate is calculated to lime, all the magnesium to carbonate, the remaining carbonate to lime, the remaining lime to nitrate, the remaining nitrate to sodium, and all the chlorides to sodium. In acid waters naturally the lime and magnesia, as well as the iron and aluminum, are calculated to the acid present in the greatest excess. These methods of calculation will give certain materials frequently found in scale formation and materials frequently supposed to cause certain characteristic troubles in either steam or domestic usage. It is possible in a purely qualitative way to judge or interpret the water on the basis of the lime and magnesium salts, for incrustation, and of the alkali salts for other troubles in boiler practice, also from the standpoint of irrigation, the various forms of the alkali salts as black and white alkali, without the necessity to use the formulas already considered.

Field Assay of Water

Mr. R. B. Dole has published in Water Supply Paper No. 151, of the U. S. Geological Survey, field methods for the assay of water in which tablets of known value are used for the determination of chlorides, carbonates, sulfates and iron. In this type of assay, a given amount of the water is taken and tablets are added to the water until certain definite reactions take place, when the number of tablets used is estimated and an approximate value obtained. The error in such work varies from 3 to 15%, but the results of the test give valuable, if not accurate, information.

BOILER ROOM CONTROL METHODS

Within recent years it has become recognized that many things happen in a boiler which makes it very inadvisable to depend absolutely upon pre-boiler control of water conditions. The actual condition of the water in the boiler brought about by operating conditions, elements of contamination, and change in return water, etc., have made it essential that testing methods for use with water collected from the boiler itself and tested immediately in or near the boiler room are very desirable. Many things have been published recently

which are slowly clearing up some of the fog which has handicapped the understanding of what goes on in the boiler. Research work relative to solubilities at high temperatures and pressures, to the proper working of mass action in boiler waters have established certain fairly definite rules the observance of which can result in a fairly general freedom from boiler water troubles. The methods from which information as to the water's condition would be gained, must be methods calling for no special agents such as intense heat, and fall into the classification of volumetric or turbidimetric methods. In the power plant the presence of excesses in the boiler water of sodium carbonate, caustic soda, the phosphate radical, the sulfate radical, and chloride radical have necessitated control tests which must be approximately accurate, although they are not tests that would compare with the methods already given, which should be considered standard. In the determination of alkalinity, both caustic and carbonate, there has been no great difference from the standard method. The use of the two indicators, phenolphthalein and methyl orange, is most general, but the quantities tested for the most rapid results are 58.3 ml. or a fraction thereof, and the acid used is N/50. The results read from the burette are directly in grains per gallon. Where other interfering agents, like phosphates, are present, the first titration using phenolphthalein is frequently modified by adding a small amount of 10% barium chloride, and then without filtering, and in the presence of the precipitate, a titration is made to the disappearance of the phenolphthalein red. For the determination of chlorides the regular chlorine method is used, but due to the fact that the sample is frequently alkaline with caustic soda, the sample must be neutralized before carrying out the titration. This chloride test gives indirect rather than direct information. It is used to watch boiler concentration on the assumption that the chlorides will concentrate uniformly regardless of treatment for calcium and magnesium impurities, and their increase over the amount present in the original supply will bear some sort of relationship to other constituents in the boiler water. As a rule additional work must be done through a competent laboratory so that several chlorine determinations can be compared in their relationship to total solids and complete boiler water composition. From this information a factor can usually be obtained for use with results of later control tests. As the alkalinity would be variable the mathematics would be as follows:

$$\text{Total Chlorine Determination as Sodium Chloride} \times F + M = \text{Total Solids},$$

where F represents the factor of relationship between chlorides and concentration, and M represents methyl orange or total alkalinity.

There is a great deal of publicity and interest in boiler water conditioning using meta-phosphates, and the presence of slight excesses of phosphate is important so that rapid methods have been worked out.

There are two, one a modification of a colorimetric method, the other a modification of the molybdate precipitation, both of which are of interest. The first method is that recommended by F. G. Straub. It is a modification of a very rapid and delicate colorimetric method, and aside from requiring five solutions, one of which is standard, and two of which must be carefully cared for, is available for field or boiler room control. The method follows:

Solutions:[36] ***Molybdic Acid Solution.***—Dissolve cold 125 g. of pure ammonium molybdate in about 2 liters of phosphate-free distilled water; add 75 ml. of concentrated H_2SO_4 slowly; make up to 2½ liters (roughly). A slight blue coloration does not hinder the use of this solution.

Hydroquinone Solution.—Dissolve 50 g. of c.p. hydroquinone in about 2½ liters of phosphate-free distilled water and add 3 ml. of concentrated H_2SO_4.

Carbonate-Sulfite Solution.—To 6 liters of distilled water add 1500 grams of com. soda ash; dissolve 225 g. of sodium sulfite in 155 ml. of water and add.

Stock Solution of Phosphate.—Pure monopotassium phosphate finely ground is dried at 105° C. for three hours, cooled, and kept in desiccator. 0.1432 gr. is dissolved in distilled water, 5 ml. of conc. H_2SO_4 added, and made up to 1 liter with distilled water; 1 ml. of this solution contains one-tenth of a milligram of PO_4.

Sulfuric Acid Solution.—Add 300 ml. of concentrated H_2SO_4 to about 2200 ml. of distilled water and label H_2SO_4.

Determination of Phosphate [36]

Measure 50 ml. of the filtered sample of boiler water into a 250 ml. volumetric flask, and add 10 ml. of sulfuric acid. To the flask 5 ml. of molybdic acid are added, followed by 5 ml. of hydroquinone solution. After five minutes, 15 ml. of the carbonate-sulfite solution are added, mixed and the flask made up to volume.

Measure 10 ml. of standard phosphate solution by a pipette into a 250 ml. volumetric flask and 20 ml. into a second flask; 40 ml. of distilled water are added to the first and 30 to the second, followed by the procedure in the determination of phosphate.

Place the flask containing the sample of boiler water between the two flasks containing the standard solutions and compare colors. If the color is lighter than the flask containing the 10 ml. it contains less than 20 p.p.m. of PO_4. If it is between the one containing the 10 ml. and the one containing 20 ml., it has between 20 and 40 p.p.m. If it is darker than the one containing 20 ml. it contains over 40 p.p.m.

Different maximum and minimum values may be established by changing the amount of standard phosphate solution used.

The presence of certain organic matter which gives marked color or high iron content will interfere with this phosphate determination. The color is not permanent; consequently, comparisons must be made within 15 minutes after the addition of sodium carbonate solution.

The second method is that recommended by the Hall Laboratories in connection with their system of boiler water conditioning. In this determination, the temperature of the sample is unimportant; in fact time can be saved by carrying out the determination on the hot sample.

Reagents:[37] ***Special Ammonium Molybdate Reagent.*** *Solution A.*—Place in a beaker 50 grams of 85% molybdic acid and mix it thoroughly with 120

[36] Control of Boiler Water Treatment to Prevent Embrittlement. F. G. Straub. Mech. Eng., p. 366–7.

[37] Phosphate Control Methods of the Hall System of Boiler Water Conditioning. Hall Laboratories, Pittsburgh, Pa.

ml. of distilled water. Add to the mixture slowly and with constant stirring 70 ml. of ammonium hydroxide (NH_4OH) sp.gr. 0.90. Filter, and then add to filtrate slowly and with constant stirring 30 ml. of concentrated nitric acid (HNO_3) sp.gr. 1.42.

Solution B.—Add 200 ml. of concentrated nitric acid (HNO_3) sp.gr. 1.42 to 480 ml. of distilled water.

When the solutions are cold add Solution *A* to Solution *B* slowly and with constant stirring. Add to the mixture 0.05 gram of ammonium phosphate $(NH_4)_2HPO_4$ dissolved in 10 ml. of distilled water. Shake and let stand for at least 24 hours, when the precipitate that has formed will have settled out. The clear solution is now ready for use.

Potassium Nitrate.—Crystalline c.p. grade. It is important that this chemical be phosphate free.

Determination of Phosphate (Buromin)

Measure out approximately 125 ml. of the boiler water to be tested and transfer it to a 250 ml. flask. Add to this one-half teaspoonful (approximately 5 grams) of the potassium nitrate and heat up to nearly the boiling point. In order to flocculate the suspended matter, the flask is then removed from the hot plate and allowed to stand for a few minutes. Then filter 100 ml. of the sample. It is important that the filtered sample be entirely free of any suspended material. If the liquid first passing through the filter is not perfectly clear, return it to the main body of the sample and continue filtration through the same paper. For this test a good grade of filter paper, such as Munktell's 1F, is essential. The 100 ml. of filtered sample is then heated to active boiling temperature and poured at boiling temperature into the Hagan Phosphate Gauge. 10 ml. of the special ammonium molybdate reagent is then added and the contents thoroughly mixed by shaking with a swirling motion. Air bubbles in the capillary stem must be eliminated by opening the stop cock and allowing a little of the liquid to flow through. This liquid is collected and returned to the gauge. If phosphate is present, a bright yellow precipitate will form, and gradually settle into the capillary stem. Allow the sample to stand for half an hour, giving the gauge an occasional swirling motion to bring all the yellow precipitate down into the stem. The depth of the yellow precipitate is read off in divisions of the calibrated stem.

Sulfate

The other determination is that involving sulfate and it is important from several angles. First it is of value in the control of embrittlement, and it is still one of the inhibiting agents depended upon most strongly and also, where other methods are employed, it is of value in connection with the use of sodium sulfite as an absorbent of oxygen for the elimination of gas corrosion. Two methods are of special interest in this case, one a turbidimetric method, the other a colorimetric method, which is quite new at this time, but which has attracted a great deal of favorable attention. In the turbidimetric method many mechanical devices are used in the obtaining of the ultimate reading which is based upon the intensity of turbidity necessary to just make impossible

the detection of light passed through a standard opening. The procedure necessary to produce the turbidity is all that will be given.

Procedure:[38] ***Reagents.***—Standard salt-acid solution, 240 grams of sodium chloride plus 20 ml. of hydrochloric acid (sp.gr. 1.19) per liter. This solution must be filtered until a zero turbidity is obtained. Barium chloride ($BaCl_2$-$2H_2O$) 20- to 30-mesh crystals.

Method.—If the sulfate content is below 50 parts per million a 50 ml. sample is taken and the test made in the 20 mm. cell. With a 50 ml. sample, 10 ml. of the standard salt-acid solution are added. If the sample contains between 50 and 100 parts per million of sulfate, a 25 ml. sample is taken in a 10 mm. cell and 5 ml. of salt-acid solution are added. To the sample is added 0.29 gram of 20- to 30-mesh barium chloride crystals measured by a standardized cup. The solution is stirred for exactly 1 minute, the plunger tube inserted, and readings are taken 4 to 6 minutes after the precipitation. An average of two readings is taken and the reading obtained compared with values from the standard curve to obtain the sulfate content of the sample. An initially turbid solution must either be filtered or a blank reading made, in terms of sulfate, before the precipitation of the barium sulfate.

The second method is known as the T. H. Q. method, and is worthy of considerable attention. The indicator and full details must be obtained from the Betz Laboratories, Philadelphia, Pennsylvania.[39]

The indicator used throughout this study was manufactured in the Betz Laboratory and considerable quantities of this material have been supplied to the field.

Detailed directions are given below for a determination of sulfate by direct titration using T. H. Q. as the indicator.

Materials and Reagents.—Standard barium chloride solution, the strength varying from 1 ml. = 1 mg. of SO_4 to 1 ml. = 50 mg. of SO_4, standardized gravimetrically. An indicator composed of disodium tetrahydrozyquinone ground with dried potassium chloride in a 1 to 300 ratio, and passing a 100-mesh screen. Ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A, or isopropyl alcohol and bromcresol green indicator (if phosphates are present). Sodium chloride crystals c.p.

Procedure A.—Carefully neutralize a 25 ml. sample containing up to approximately 2000 p.p.m. of SO_4 with approximately 0.02 N hydrochloric acid until just acid to phenolphthalein. The temperature of the sample should be below 35° C. and it is advisable to work between 20° and 25° C. Add either 25 ml. of ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A or isopropyl alcohol. Introduce the T. H. Q. the amount to be determined from Table I. It is best to use a small cup to measure the mixture. Swirl flask to dissolve the T. H. Q.; the solution will be colored a deep yellow. Titrate with standard barium chloride solution, the strength to be employed depending on the approximate sulfate content of the sample, in accordance with Table 1. Add the standard barium chloride at a steady dropping rate with a constant swirling of the flask until the yellow color changes to a rose. The rose color

[38] Turbidimetric Determination of Sulfate in Water. R. T. Sheen, H. L. Kahler, and E. M. Ross, W. H. & L. D. Betz, Philadelphia, Pa.

[39] Direct Titration of Sulfates. R. T. Sheen and H. L. Kahler, W. H. & L. D. Betz, Philadelphia, Pa.

TABLE I

PROCEDURE REQUIREMENTS

Approximate SO_4 Concentration in p.p.m. (1)	Quantity of THQ Indicator gms. (2)	Dippers THQ Indicator (3)	1 ml. $BaCl_2$= in mg. SO_4 (4)	1 ml. $BaCl_2$= in p.p.m. SO_4 (5)
* up to 100	0.1	½	1	40
* 100–1,000	0.2	1	1	40
1,000–2,000	0.2	1	4	160

* Subtract 0.1 ml. as a blank in titration.

should appear, throughout the body of the solution and not as spots of color. This point is taken as the end point.

Procedure B (sulfate range from 2000 to 30,000 p.p.m.).—Add solid sodium chloride to the sample in an approximate amount as given in Table II. The procedure is the same as in *A* for neutralization and titration.

TABLE II

PROCEDURE REQUIREMENTS

Approximate SO_4 Concentration in p.p.m. (1)	Quantity of THQ Indicator gms. (2)	Dippers THQ Indicator (3)	1 ml. $BaCl_2$= in mg. SO_4 (4)	1 ml. $BaCl_2$= in p.p.m. SO_4 (5)	Sodium Chloride crystals required gms. (6)
2,000– 4,000	0.4	2	10	400	2
4,000–10,000	0.4	2	10	400	4
10,000–20,000	0.6	3	50	2,000	8
20,000–30,000	0.8	4	50	2,000	8

Procedure C (with phosphate ion present up to 60 p.p.m.).—Carefully neutralize a 25-ml. filtered sample with approximately 0.02 N hydrochloric acid until just acid (yellow range) to bromcresol green (approximately pH 4). Follow procedure as in *A* or *B*; no correction will be required for the phosphate ion present.

RAPID METHODS FOR WATER ANALYSIS

These methods are of sufficient accuracy for field work study of underground waters, where rapid methods are desired. The outline suggested by F. G. Tickell in his report to the California State Mining Bureau [40] furnishes the basis of the methods considered.

The following determinations are of special interest:

Positive Radicals—calcium, magnesium, sodium and potassium.

Negative Radicals—chloride, sulfate, bicarbonate, carbonate, hydroxide.

[40] F. G. Tickell—Summary of Operations—California Oil Fields—Tenth Annual Report, Vol. 10, No. 6, Dec., 1924.

Colloids—iron oxide, alumina, silica.
Loss on Ignition—organic matter, CO_2.
Total Dissolved Solids.

Special Reagents Required: ***A. Standard Sodium Chloride Solution.***—Dissolve 1.648 grams of dry NaCl in a graduated liter volumetric flask and dilute to exactly 1000 ml. with distilled water.

1 ml. contains an equivalent of 1 mg Cl.

B. Standard Silver Nitrate Solution.—Dissolve 4.8 grams of $AgNO_3$ crystals in a liter volumetric flask with distilled water and dilute to 1000 ml. Standardize as follows:

Transfer 25 ml. of the sodium chloride solution to a porcelain dish. Add 0.5 ml. of 10% solution of neutral K_2CrO_4 solution and dilute to 100 ml. with distilled water. From a 50 ml. burette, add with constant stirring the silver nitrate reagent until a faint, but persistent red color (Ag_2CrO_4) is obtained.

Divide 25 by the ml. $AgNO_3$ required; the result is the mg. Cl equivalent of 1 ml. of the $AgNO_3$ reagent. Record this on the bottle.

Reagents *A* and *B* are used in chlorine determinations.

C. Standard Acid—N/10 Solution.—Details of standardization are given in the text. Three ml. of the desk H_2SO_4 (sp.gr. 1.84—93% solution) diluted to 1000 ml. is approximately a N/10 solution. 0.265 g. Na_2CO_3 will require exactly 50 ml. of acid for its neutralization. (Methyl orange or alizarine indicator.) In an Erlenmeyer flask place a carefully weighed (0.2–0.25 g.) dry, pure Na_2CO_3. Titrate with the acid. Calculate the N/10 alkali equivalent volume by dividing the weight of the salt used by 0.0053 and divide this by the ml. of the acid necessary. The result is the normality of the acid. Multiply all the acid titrations by this factor to get the true N/10 volumes.

Reagent *C* is used in carbonate and alkalinity determinations.

D. Barium Chloride Reagent, N/4 Solution.—Dissolve 30.6 grams of $BaCl_2 \cdot 2H_2O$ crystals in water and dilute to 1000 ml. in a volumetric flask using distilled water. One ml. of this reagent is equivalent to about 0.012 g. SO_4. Standardize the reagent as follows: By means of a pipette draw out 25 ml. and precipitate the barium as $BaSO_4$ with dilute H_2SO_4 (see determination of barium). Filter, wash, ignite in a weighed crucible and weight the $BaSO_4$. Multiply by 0.4115 to obtain the equivalent SO_4. This result divided by 25 will give the equivalent SO_4 per ml. of the reagent. Record mg. per ml.

E. Standard Potassium Chromate Reagent—N/4 Solution.—Dissolve 24.5 grams of the crystallized salt in water and make to 1000 ml. in a volumetric flask. One ml. of this reagent is equivalent to 1 ml. of the $BaCl_2$ reagent. To get the exact value proceed as follows: Take 25 ml. of the $BaCl_2$ reagent in an Erlenmeyer flask; neutralize with NH_4OH; heat to boiling and add 20 ml. of the K_2CrO_4 reagent from a 50 ml. burette, continue the titration with 0.5 ml. portions, removing the flask after each addition, allowing to settle and observing whether the clear upper layer of solution is colored yellow. Continue until a faint yellow color due to a drop or so excess of the reagent over that required by the Ba. The ml. required divided into 25 and multiplied by the SO_4 factor of the $BaCl_2$ reagent gives the SO_4 value of 1 ml. of the K_2CrO_4 reagent. Record the mg. SO_4 per ml.

NOTE.—Since suspended $BaCrO_4$ obscures the end point, the following procedure is recommended:—As the end point is approached, filter off and examine 5 ml. portions, returning to the main solution the portion each time until the end point is reached.

F. Alkali Reagent—N/10 Solution.—Dissolve 5.3 grams of pure Na_2CO_3 and 4.8 grams of stick NaOH in water and dilute to exactly 2000 ml. with distilled water in a two liter measuring flask. Standardize against the standard acid solution using alizarine or methyl orange indicator. Record the exact normality factor.

G. Indicators.

Alizarine.—One gram pure alizarine paste mixed with 200 ml. of distilled water. One drop is used in the titrations. Color is violet with alkaline solution, pale lemon with neutral or acid solutions.

Methyl orange.—(See text.)

Phenolphthalein.—(See text.)

H. Ammonium Oxalate Solution.—Saturated solution.

I. Permanganate Reagent N/10.—(See text.) 1 ml. = 0.002 g. Ca.

Methods of Procedure: ***Chloride Determination.***—By means of a 100 ml. pipette transfer that volume of water to be examined to a porcelain dish. Add a few drops of 10% potassium chromate indicator solution and titrate with silver nitrate reagent adding this until a faint but permanent red color (Ag_2CrO_4) is obtained. Report results in mg. Cl per liter. (Parts per million.)

Carbonate (CO₃) Bicarbonate (HCO₃) and Hydroxyl (OH) Determination.—Place, by means of a pipette, 100 ml. of the water in a beaker or porcelain dish; add a few drops of phenolphthalein indicator. A pink color indicates the presence of a carbonate. A colorless solution indicates its absence.

If a pink color is obtained titrate with N/10 acid until the pink color disappears; read the burette and record the result as ml. P.

TABLE FOR CALCULATION

Indicator and Titration	HCO_3^-	$CO_3^=$	OH^-
P equals zero	ml. M×6.1×f.	Nil.	Nil.
P less than ½ M	ml. M−2(ml. P)×6.1×f.	2(ml. P)×3×f.	Nil.
P equals ½ M	Nil.	2(ml. P)×3×f.	Nil.
P is greater than ½ M	Nil.	2(ml. M−ml. P)×3×f.	2(ml. P)−ml. M×1.7×f.
P equals M	Nil.	Nil.	ml. P or ml. M×1.7×f.

f. is the factor for the normality of the acid.
1 ml. N/10 acid = 6.1 mg. HCO_3 3 mg. CO_3 1.7 mg. OH.

To the colorless solution add a couple of drops of methyl orange indicator and continue the titration with the N/10 acid until the yellow color changes to orange. Read the burette and record the ml. as ml. M. (M here is the total ml. of acid including P.)

NOTES.—In the table the ml. figures represent mg. of the equivalent HCO_3, CO_3 or OH as the case may be. The ml. are converted to N/10 value by multiplying by the factor f. and then by the figure in question. 6.1 for mg. HCO_3, 3 for mg. CO_3, and 1.7 for mg. OH.

In general the CO_3 and OH are not found in waters that contain appreciable amounts of the alkaline earths (Ca and Mg). The ratio of carbonate to bicarbonate in water containing very small amounts of Ca or Mg is influenced by the amount of dissolved CO_2 in the solution. A high CO_2 content indicates that HCO_3 predominates. If this is low the normal carbonate is present. A fresh sample may show HCO_3 and no CO_3, but the loss of CO_2 will occur and CO_3 will be found with HCO_3.

Sulfate Determination.—The volumetric procedure depends upon the insoluble $BaSO_4$ forming and settling rapidly when $BaCl_2$ solution is added to the sulfate. The reagent is added in excess and the excess determined by titration with K_2CrO_4 with formation of $BaCrO_4$. A slight excess of the chromate reagent becomes evident by coloring the solution yellow, best seen when the yellow $BaCrO_4$ has settled slightly or by filtering from $BaCrO_4$. See Note under E.

$$MSO_4 + BaCl_2\ (xs) = MCl_2 + BaSO_4 + (xs\ BaCl_2).$$
$$BaCl_2 + K_2CrO_4\ (xs) = BaCrO_4 + (xs\ K_2CrO_4\ \text{yellow solution}).$$

Procedure.—Pipette 100 ml. of the water into a beaker and make faintly acid with HCl (litmus paper) and heat to boiling. While boiling add from a burette the standard $BaCl_2$ reagent in small portions at a time allowing to settle with each addition until all the sulfate has been precipitated and the reagent is in slight excess. Record the ml. used.

Cautiously neutralize the solution with NH_4OH (carbonate free), heat to boiling and titrate the excess of the $BaCl_2$ with K_2CrO_4 standard reagent according to the method under E of Special Reagents. See Note under E.

The SO_4 value of $BaCl_2$ minus the SO_4 value of K_2CrO_4 titrations (ml. $BaCl_2 \times SO_4$ value minus ml. $K_2CrO_4 \times SO_4$ value) is the SO_4 content of the 100 ml. sample of water. Report mg. per liter. (Parts per million.)

Optional Procedure.—Acidify the solution with HNO_3 and heat to boiling. Cool and neutralize with NaOH solution using as an indicator just sufficient amount of litmus solution to detect end point avoiding an excess. Add a 10% solution of $AgNO_3$ dropwise until all the chloride is precipitated and then a few drops in excess; now add a slight excess of standard barium nitrate (standardized as was the $BaCl_2$ reagent—mol. wt. 261.4 $Ba(NO_3)_2$). Titrate this excess with standard potassium chromate. A red color (Ag_2CrO_4) will indicate the approximate end point. Dissolve the Ag_2CrO_4 by adding NH_4Cl, heat to boiling, and continue the titration with K_2CrO_4 until the faint yellow color is obtained as in the first method. Subtract the SO_4 value of the chromate from the SO_4 value of the barium nitrate to obtain the SO_4 of the water. Report mg. per liter. (Parts per million.)

Alkaline Earths

Calcium and Magnesium Determination.—Calcium and magnesium here are determined jointly by precipitating with the mixed reagent Na_2CO_3 and NaOH (the latter necessary for the complete precipitation of Mg). The excess of the alkali is determined by titration with a standard acid. The two are reported as calcium.

Procedure.—Place 100 ml. of the water in an Erlenmeyer flask and add 25 ml. of the standard alkali reagent (F); boil, filter, and wash. To the filtrate containing the excess of the alkali reagent add a drop of the alizarine indicator

and titrate (best conducted in an Erlenmeyer flask) the alkali, adding a few drops of the acid in excess. Boil to expel the CO_2 and determine the excess of the acid by back titration with the standard alkali to the yellow neutral point, best obtained by adding the alkali to a faint pink and back to yellow with a drop of standard acid.

Calculation.—If *A* is the total alkali reagent added, i.e., the 25 ml. and the back titration for acid neutralization; and *B* is the acid titration (both being converted to their exact equivalents—ml. in terms of 0.1 N), then *A* minus *B* is the amount of alkali reagent required in the precipitation of Ca and Mg.

One ml. of 0.1 N (i.e., N/10) alkali reagent is equivalent to 0.002 g. Ca.

Express the results in mg. per liter.

Magnesium Determination.—Concentrate 100 ml. of the water to about a fourth of its volume. Acidify with HCl and expel the CO_2 by boiling. Cool, add a few drops of phenolphthalein and neutralize the free acid with NaOH solution. Now from a burette add a measured amount of standard NaOH reagent (0.1 N) in amount sufficient to precipitate all the Mg present and a slight excess. Estimate the total volume present and add twice its volume of 95% alcohol, $Mg(OH)_2$ precipitates. Transfer to a 250 ml. volumetric flask, make up to 250 ml. with 1 : 1 alcohol. Filter off 70–80 ml. and take 50 ml. of this. Titrate the excess of NaOH with standard acid and multiply by 5. Calculate the 0.1 N NaOH required by Mg. 0.1 N NaOH will precipitate per ml. 0.00122 g. Mg.

Note.—In the determination of magnesium, elements forming insoluble hydroxides, under the conditions for magnesium hydroxide precipitation, should be removed previous to the determination of magnesium. The common interferences are iron, aluminum and calcium.

Calcium Determination.—Concentrate 100 ml. of the water to about half its volume if the water is comparatively soft or determine directly if hard. Details of the oxalate-permanganate method are given in the text.

Alkali Determination.—These are calculated by difference, it being assumed that the amount of other radicals in the solution is negligible.

Consult table following. Multiply each radical value by its proper reaction coefficient and balance the + and − reacting values; the difference will be the reacting value of sodium in the solution. Divide this value by the reaction coefficient for sodium to obtain the mg. of sodium. Calculate the mg. per liter.

REACTION COEFFICIENTS

Positive	Reaction Coefficients		
	r	Negative	*r*
Na	0.0435	SO_4	0.0208
Ca	0.0499	Cl	0.0282
Mg	0.0822	CO_3	0.0333
		HCO_3	0.0164
		OH	0.0588

IRRIGATING WATERS

When a water supply is to be used for the purpose of irrigation, it is necessary to bear in mind the fact that there are certain impurities which, if present in large enough quantities, or due to imperfect drainage, are allowed to accumulate in the soil, will have a most detrimental action on growing crops. Due to solubility, these are usually soda salts. They are objectionable unevenly. Sodium carbonate seems the most dangerous and sodium sulfate the least. Not a great deal has been published on the subject, though there is one government bulletin [41] and one article by Stabler.[42] Growing out of the latter the following tables which are of value are offered.

Irrigating Waters

Alkali Coefficient

(*a*) When $Na - .65\ Cl$ is zero or negative,

$$\text{Alkali coefficient, } k = \frac{2040}{Cl}.$$

(*b*) When $Na - .65\ Cl$ is positive, but not greater than $.48\ SO_4$,

$$\text{Alkali coefficient, } k = \frac{6620}{Na + 2.6\ Cl}.$$

(*c*) When $Na - .65\ Cl - .48\ SO_4$ is positive,

$$\text{Alkali coefficient, } k = \frac{662}{Na - .32\ Cl - .43\ SO_4}.$$

Classification on basis of alkali coefficient:

Alkali Coefficient	Class	Remarks
More than 18...	Good...	Have been used successfully for many years without special care to prevent alkali accumulation.
18 to 6.....	Fair....	Special care to prevent gradual alkali accumulation has generally been found necessary except on loose soils with free drainage.
5.9 to 1.2.....	Poor....	Care in selection of soils has been found to be imperative and artificial drainage has frequently been found necessary.
Less than 1.2....	Bad....	Practically valueless for irrigation.

It must be borne in mind that the dangerous characteristics of a water have a close relationship to the drainage, and with perfect drainage waters that would ordinarily be condemned, can sometimes be used without serious results.

[41] Some Mutual Relations between Alkali Soils and Vegetation, Thomas H. Kearney and Frank K. Cameron, U. S. Department of Agr., Report No. 71.

[42] Stabler, Herman, "The industrial application of water analyses." Water-Supply Paper U. S. Geol. Survey No. 274, p. 179.

THE MICROSCOPICAL EXAMINATION OF WATER SUPPLY

IMPORTANCE OF THE DETERMINATION

From the standpoint of palatability and of the esthetic character of water supply there is no more important examination than the microscopical analysis. This examination discloses and measures the minute animal and plant life that is present in all surface waters and in some well waters.

Large amounts cause an unsightly turbidity and even relatively small quantities frequently cause complaint because of a scum produced when bath tubs are filled with hot water or of a stain left upon the sides of the white porcelain. The water of swimming pools, if unfiltered, may be unsightly. Industrial enterprises may be affected, for example the staining of clothes in laundries and interference with the manufacture of correct colors by dye manufacturers and with the dyeing of goods by the dyers. Photography may also be influenced.

The presence of certain types of microscopic organisms frequently serves to identify the source of a water, or indicate from what particular reservoir a supply may be drawn. In the case of New York City which serves to certain districts of Manhattan Borough water from the Croton supply, to other sections water from the Catskill supply and mixtures to others, the supply in any one section may be identified by the organisms as Catskill, Croton or a mixture. Again samples from cellars, excavations and conduits are frequently analyzed to determine whether the source is city water, sewage, or ground water. If microscopic organisms are present city water or sewage must be responsible and the chemical analysis and odor usually eliminate or indicate sewage. The contamination of a well supply by surface waters may be indicated by the presence of microscopic organisms.

The amounts of microscopic organisms bear a direct relationship to the various forms of nitrogen determined in the chemical analysis and frequently explain changes in these determinations.[1] As these growths increase free ammonia and nitrate decrease and albuminoid ammonia increases and as the growths decrease the reverse relationship holds.

The operation of filter plants, particularly the mechanical type, is much interfered with by heavy growths of microscopic organisms, the network of the latter interfering with the gelatinous formation of aluminum hydroxide in mechanical filters and the bacterial jelly of slow sand filters, although certain types of the diatoms may assist in the latter case.

Chapter contributed by F. E. Hale, Ph.D.

[1] "The Significance of Nitrogen in its Various Forms in Water Supply." F. E. Hale, Proc. Am. W. W. Assoc., 1908, pages 323–327.

By far the most important reason for determining microscopic organisms is their connection with disagreeable, sometimes vile, tastes and odors in water supply. Those so-called littoral growths, which are attached to the banks or bottoms of reservoirs, and which attract the quickest attention are not concerned as a rule. The trouble is caused by minute floating forms, which manufacture essential oils or perfumes like those of flowers. Exceedingly minute amounts produce pleasant aromatic geranium or grassy odors which become fishy, oily, pungent or vile in larger amounts or upon decay of the plant growths. Particular genera may frequently be identified by the odor by those who are trained.

Three groups of odors are distinguished:

Aromatic (geranium) caused by Diatomaceae.
Grassy caused by Cyanophyceae.
Fishy caused by Chlorophyceae and a few Protozoa.

The following table as given by Whipple [2] in "The Microscopy of Drinking Water" contains those organisms which have been at one time or another in sufficient quantity in a water supply to produce characteristic odors.

Group	Organism	Natural Odor
Aromatic odor	Diatomaceae:	
	Asterionella	Aromatic, geranium, fishy
	Cyclotella	Faintly aromatic.
	Diatoma	Faintly aromatic.
	Meridion	Aromatic.
	Tabellaria	Aromatic, geranium, fishy.
	Protozoa:	
	Cryptomonas	Candied violets.
	Mallomonas	Aromatic, violets, fishy.
Grassy odor	Chlorophyceae:	
	Dictyosphaerium	Grassy.
	Cyanophyceae:	
	Anabaena	Moldy, grassy, nasturtium, green-corn.
	Aphanizomenon	Grassy.
	Coelosphaerium	Grassy, sweet.
	Clathrocystis	Grassy, sweet.
	Cylindrospermum	Grassy.
	Rivularia	Moldy, grassy.
Fishy odor	Diatomaceae:	
	Asterionella	Fishy in large numbers.
	Tabellaria	Fishy in large numbers.
	Chlorophyceae:	
	Dictyosphaerium	Faintly fishy, also grassy.
	Eudorina	Faintly fishy.
	Pandorina	Faintly fishy.
	Volvox	Fishy.
	Protozoa:	
	Bursaria	Irish moss, salt marsh, fishy.
	Ceratium	Fishy.
	Dinobryon	Fishy, like rock-weed.
	Glenodinium	Fishy.
	Mallomonas	Fishy, also aromatic.
	Peridinium	Fishy, like clam-shells.
	Synura	Cucumber, fishy, muskmellon, bitter taste.
	Uroglena	Fishy and oily.

[2] With some additions by the author.

In New York City's supplies, despite the diversity of its sources, the only organisms which have given offense from odors have been *Asterionella, Tabellaria, Volvox, Dictyosphaerium, Anabaena, Aphanizomenon* (with admixtures of *Coelosphaerium, Clathrocystis, and Microcystis*), *Ceratium, Dinobryon, Peridinium, Synura, Uroglena,* and *Crenothrix.*

Asterionella, when present in 500 to 1000 standard units per cubic centimeter, produces a slightly aromatic odor. At 1000 units, rarely less, the odor is distinctly similar to the odor of the geranium. The odor increases in intensity with increase in numbers until several thousand produce a fishy odor. The fishy odor is also produced when smaller quantities die.

Tabellaria, and similarly *Asterionella,* in very small amounts produces an earthy odor (also produced by large amounts of *Synedra*), passing through the aromatic, geranium and fishy stages with about the same relative quantities of organisms as *Asterionella.* At times the odor of *Tabellaria* has suggested illuminating gas, no other organisms being present. In the spring of 1919 extensive complaints of fishy taste in the Catskill supply were occasioned in New York City by only 700 units of *Tabellaria.* This was the result of chlorination with liquid chlorine at Kensico reservoir. The odor was not noticeable in the water above the chlorination plant but appeared first just below the plant. Chlorination killed the organism, setting free the odorous principle.

Anabaena and *Aphanizomenon,* when present in 500 to 1000 units, produce a faintly grassy odor like freshly-cut grass. With larger numbers the odor becomes pungent like nasturtium, or even onions. In large numbers, or when decaying, the odor is of vile, pigpen character. In the spring of 1918 from 500 to 800 units of *Aphanizomenon* in the Croton supply of New York City caused numerous complaints of an oily brown scum when bath tubs were filled with hot water. These complaints came chiefly from high class apartment houses.

Uroglena produces an oily fishy taste and odor, first noticeable in probably 500 to 1000 units. In larger quantities it is very disagreeable. The flavor is that of cod-liver oil. Chlorine has an influence on this organism also.

Synura has caused trouble in as small amount as 50 units. The odor is variously described as like cucumber, muskmellon, etc. It leaves a bitter aftertaste. Chlorine intensifies the trouble so that only a few units are noticeable.

Dictyosphaerium, about 700 units, under influence of chlorine has produced a grassy or pungent nasturtium odor.

Troublesome organisms occur chiefly in surface waters. Occasionally well waters containing iron or manganese cause trouble from growths of *Crenothrix* and associated forms which clog pipes and cause an unsightly turbid discolored water. Well strainers become clogged so as to prevent proper yield of water.

Microscopic organisms apparently do not affect the health. Possibly the taste and odor at times produce nausea or distaste for food. It would take 12,000 units of *Asterionella* per cubic centimeter to add a milligram of solid matter to a glass of water.

SAMPLING FOR ANALYSIS

In sampling water for microscopical analysis precautions should be taken that the sample be representative and fresh. Water from a tap should be allowed to run to avoid heated stagnant water. Samples from a pond or reservoir should not contain surface scum nor littoral growths. Deep samples are best taken by the method usually employed for dissolved oxygen samples. A quart bottle is fastened by clamps to the side of a two-quart bottle in a water sampler. The bottles are fitted with two-hole rubber stoppers. Glass tubing is arranged as follows: A straight tube, projecting slightly above the stopper, extends to the bottom of the quart bottle. A bent tube is made flush with the underside of the same stopper and connected by a short piece of stiff rubber tubing to a bent glass tube extending through the stopper of the two-quart bottle to its bottom. A straight tube, flush with the underside of the stopper of the two-quart bottle, extends above the stopper from eight to ten inches in order to make a difference of head between the inlet and outlet tubes. The bottles are lowered quickly to the required depth by a marked and measured rope. Watch is kept for bubbles of air which rise to the surface of the water, sometimes several feet away, until bubbling ceases, which takes two to four minutes. Both bottles must be completely filled before raising, otherwise the sample may be from some other depth than that desired. The water enters the small bottle first and, as it only takes one half minute to lower the apparatus to the desired depth and at least two minutes for both bottles to fill, the smaller bottle is filled with the last water to enter which is from the desired depth. If the large bottle were not completely filled, the bottles would be filling while being drawn up and the water of the small bottle would represent some unknown depth. (See Fig. 291.)

Fig. 291.—Sampling Apparatus for Deep Samples.

SEDGWICK-RAFTER METHOD OF EXAMINATION

Apparatus Required

A microscope (not necessarily high priced).
Eyepieces—One inch (25 mm.) and one half inch (12 mm.).
Objective—Two thirds inch (16 mm.) and one sixth inch (4 mm.).
Ocular micrometer—Fitted to one-inch eyepiece.

This is ruled with a square of such size that used with a one-inch eyepiece and two-thirds inch objective the tube length of microscope may be adjusted so that the area viewed on the stage will be one square millimeter. The tube length is adjusted by making the square in the eyepiece coincide with a stage micrometer. The large square is usually divided into quarters, one quarter into 25 small squares and one of the latter into 25 tiny squares; each of the last represents an areal unit of measurement, 400 square microns (20 microns to the side). A micron equals .001 mm.

A stage micrometer—graduated usually to tenths of a millimeter.

Sedgwick-Rafter Counting Cell—a thick slide to which is cemented a brass rim with internal dimensions of length 50 mm., width 20 mm., and depth 1 mm. It has an area of 1,000 square millimeters and a capacity of 1 cubic centimeter. Its depth only must be exact. Several should be provided.

Thin cover glasses, 55 mm. by 25 mm., to use as covers for the cells.

One cubic centimeter pipettes (regular bacteria pipettes will do).

Five cubic centimeter pipettes, volumetric.

A small glass jar of distilled water—for rinsing cells and coverglasses.

Lintless cloth or handkerchiefs—for drying cells and coverglasses.

One-inch test tubes of heavy glass (bacteria dilution tubes).

Five-eighths-inch test tubes of heavy glass (bacteria media tubes).

Sedgwick-Rafter funnels. These are cylindrical, 2-inch diameter, sloping toward the bottom to a neck of $\frac{1}{2}$-inch diameter. The distance from top to slope is 9 inches, length of slope 3 inches, length to bottom $2\frac{1}{2}$ inches.

A small glass jar of distilled water—to furnish water for concentrates.

Perforated rubber stoppers—to fit one half inch tube of funnel.

Silk bolting cloth No. 15x.

Steel punch—to make $\frac{3}{8}''$ diameter discs of bolting cloth for rubber stoppers.

White sand, 60 to 120 mesh, i.e., passing a sieve of 60 mesh to the inch and retained on 120 mesh (Berkshire sand or ground quartz).

Support for battery of funnels.

A small wooden mustard spoon—to measure sand.

Volumetric flasks, 200 ml. capacity.

Test-tube racks.

Record books designed for microscopic examinations.

For field work, which is sometimes of importance due to destruction of organisms in transit, a folding microscope and a metal sling filter are useful but not necessary.

Procedure.—The actual procedure of examination is simple. Familiarity with the various genera is essential. In the limited space of this chapter it is impossible to picture the thousands of forms that exist. The best working book, containing also plates, is "The Microscopy of Drinking Water" by George C. Whipple. (Revised by Fair and Whipple.) References to other books showing plates will be found at the end of the chapter.

Moisten the small end of rubber stopper with water so as easily to pick up a disc of silk bolting cloth from the table and insert tightly into the funnel. Fill the mustard spoon with prepared sand and drop into funnel making one-half inch layer. Pour in 200 ml. of the water to be examined from a flask and

allow to filter, thus concentrating the organisms upon the sand. Do not allow the sand to stand until drained dry. Slight suction may be carefully applied to clogged filters. Remove funnel, hold in a slanting position and carefully remove stopper and insert the end of funnel into a one-inch test tube. Wash sand and contents into the test tube by 5 ml. of distilled water, running the latter quickly around the sides of the funnel. Shake water and sand, settle a few moments and decant liquid into the smaller ($\frac{5}{8}$ inch) test tube. A rack of these concentrates may be prepared at one time for examination. Rinse three or four Sedgwick-Rafter cells and coverglasses in distilled water and carefully dry with lintless cloth. Place coverglasses slantingly across cell so as to leave air space at diagonally opposite ends. Run 1 ml. of concentrate into one corner of cell, air leaving at the opposite corner, and slide coverglass into position to close cell. Allow cells to stand at least five minutes before examining so that organisms will have an opportunity to settle completely, as most of them will. This step is very important. While examination is being made of one cell, others will be settling. Thus at least three should be kept going in rotation when many samples are to be examined.

Examine under the microscope with one-inch ocular containing micrometer and $\frac{2}{3}$-inch objective and proper tube length as previously determined. Estimate the number of standard units of each organism present in an entire field within the large square of the eyepiece and note on record sheet. Area only is taken into account. Forms like *Asterionella*, *Diatoma*, *Synedra*, *Tabellaria* may be counted and multiplied by a factor to get the number of units—thus each arm of *Asterionella* may be estimated as equal to one half unit. Filamentous forms like *Melosira*, *Anabaena*, *Aphanizomenon*, *Oscillaria* may be counted in lengths of five units (one-tenth of side of large square) and the total length divided by the number of filaments laid side by side that it would take to measure five units. The quotient multiplied by 25 gives the number of units in the field. *Synedra* in "fine-tooth-comb form," *Fragillaria*, *Uroglena*, *Synura* and bulky forms may be quickly compared with a 25-unit square and the number of units in the field estimated. The above method of estimating units is quicker than it reads and tends to eliminate largely the personal element from the count. After the bottom of the slide has been counted, focus should be changed to the top layer and Cyanophyceae, which float, estimated, that is *Anabaena*, *Aphanizomenon*, *Clathrocystis*, *Microcystis*, *Coelosphaerium*, etc.

Standard Methods of the American Public Health Association and Am. Water Works Association require 10 fields of the 1000 to be examined. In ordinary practice, however, a careful count of five representative fields is sufficient, choosing fields through the middle of the cell at each end, the center and half way between. After counting, a search of the cell, particularly the edges, is made for missed forms, especially Crustacea which swim to the edges to get air and Protozoa like *Uroglena*. The latter are frequently rolling around in the body of the cell. *Anabaena*, *Uroglena* and *Dinobryon* commonly break up and disintegrate in the absence of air and must be recognized in such condition. The process of disintegration frequently may be witnessed under the microscope. Sometimes disintegration occurs in transit.

On the record sheet, the amounts of units of each organism are summed up for the number of fields examined and multiplied by a factor to find the total

units as referred to the original water. The latter amounts are summed to find the total units of organisms per cubic centimeter.

If the quantities recommended in this chapter are used the factor is found as follows:

The ratio of total cell to counted fields is $\frac{1000}{5} = 200.$

The concentration is $\frac{200 \text{ cc.}}{5 \text{ cc.}} = 40.$

The final factor is then $\frac{200}{40} = 5.$

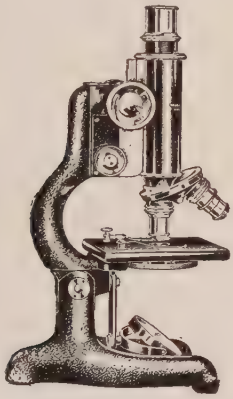


FIG. 292.—Microscope for Microscopical Examination.

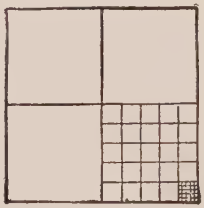


FIG. 293.—Ocular Micrometer. Smallest square is one unit.

Large crustacea found only around the edges and not distributed through the cell should have their total units divided by the concentration rather than multiplied by the factor in referring the count to the original water.

In addition to the count an examination of the original sample in the bottle by naked eye is often useful in detecting such forms as *Uroglena*, *Cyclops*, etc., and in forming a general estimate of the amounts of organisms present.

Many errors may enter into the quantitative estimation of microscopic organisms. The sample bottle should be inverted to distribute the forms, as some float and others settle. Organisms may adhere to the sides of the funnel or to the sand. Others may pass through the sand and some may disintegrate. One of the greatest errors is caused by uneven distribution through the cell when organisms are not numerous. Whipple states that the total error does not usually exceed 10%. The author of this chapter believes this figure is too conservative and unavoidably so owing to the large personal element. However results are usually comparative at any one laboratory.

Tabular Outline Identification of Forms

Sample..... *Date of Collection*..... *Number*.....
Examined by..... *Date of Examination*..... *Concentration*.....

No. of Square	1	2	3	4	5	6	7	8	9	10	Total	Standard Units Per C. C.
DIATOMACEAE:												
Asterionella		1	2		1						4	20
Cyclotella												
Diatoma												
Fragilaria												
Melosira	3	5	4	10	2						24	120
Navicula												
Stephanodiscus	1	1	1	1	1						5	25
Synedra		20		5							25	125
Tabellaria					4						4	20

List of Organisms

CHLOROPHYCEAE:
Closterium
Conferva
Eudorina
Pandorina
Pediastrum
Protococcus
Scenedesmus
Spirogyra
Staurastrum

CYANOPHYCEAE:
Anabaena
Aphanizomenon
Clathrocystis
Coelosphaerium
Microcystis
Oscillaria

SCHIZOMYCETES, ETC.:
Crenothrix
Mold Hyphae

PROTOZOA:
Ceratium
Dinobryon
Glenodinium
Mallomonas
Peridinium
Synura
Trachelomonas
Uroglena
Vorticella

ROTIFERA:
Anuraea
Polyarthra
Synchaeta

CRUSTACEA:
Bosmina
Cyclops
Daphnia

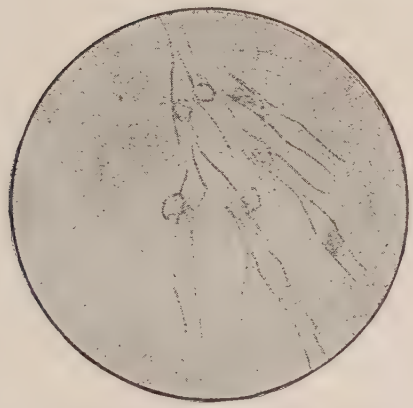
OTHER ORGANISMS:
Anguillula
Acarina

TOTAL ORGANISMS:
Amorphous Matter
Miscellaneous Bodies
Sponge Spicules

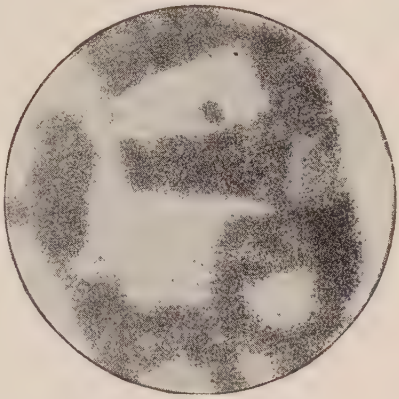
Amorphous matter comprises organic debris due largely to broken-down microscopic organisms and zoöglea.[3] It is usually of little importance but in connection with consumption of dissolved oxygen in reservoirs just below the thermocline and at the bottom it has been shown to have importance.[4]

[3] The estimation should not usually include mineral matter, silt, precipitated iron, etc., as indicated in "Standard Methods of the American Public Health Association," since this can serve no apparently good purpose.

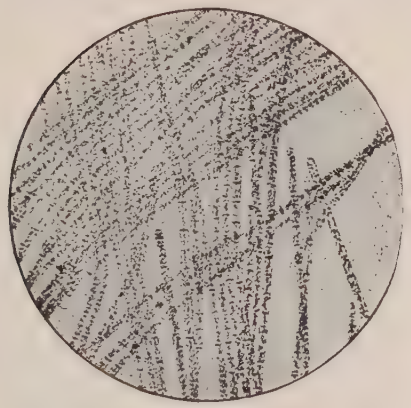
[4] "Thermocline Studies at Kensico Reservoir," Hale and Dowd, Jour. Ind. Eng. Chem., Vol. 9, page 81.



1. *Dinobryon*, magnification 250.

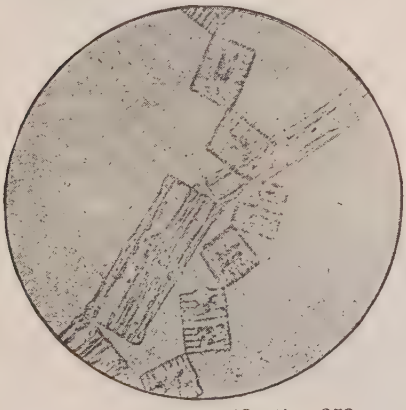


2. *Clathrocystis*, magnification 250.

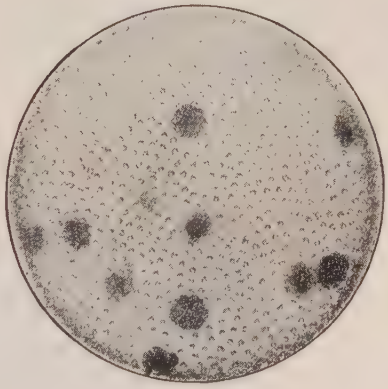


3. *Aphanizomenon*, magnification 250.

4. *Anabaena*, magnification 250.

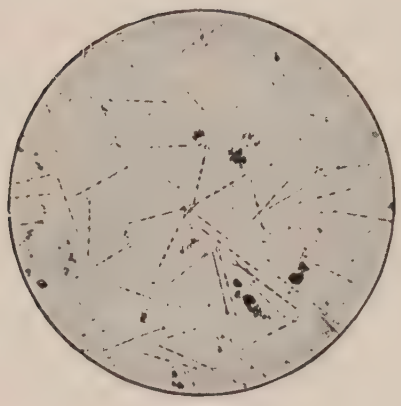


5. *Tabellaria*, magnification 250.
2, 3, 4. grassy to pigpen odor.

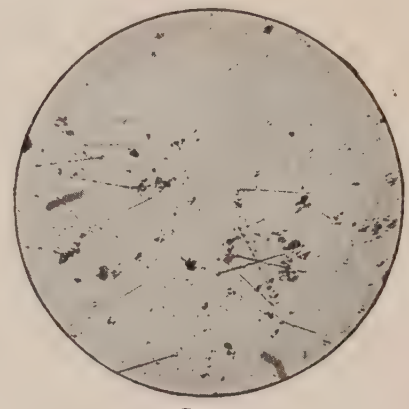


6. *Volvox*,[5] magnification 100.
5. Aromatic geranium to fishy odor.
1, 6. Fishy odor.

[5] Entire figure is a single colony and dark spots are young volvoces in the colony.

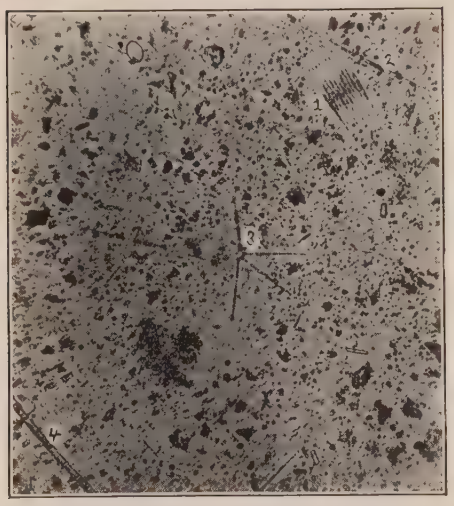


A

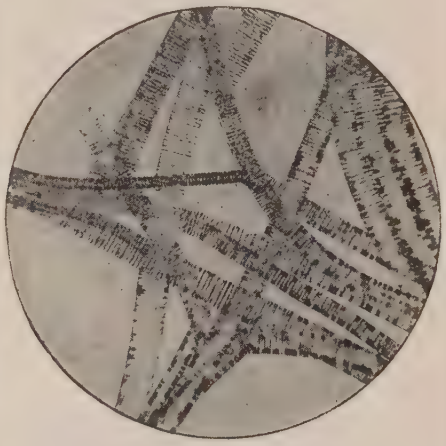


B

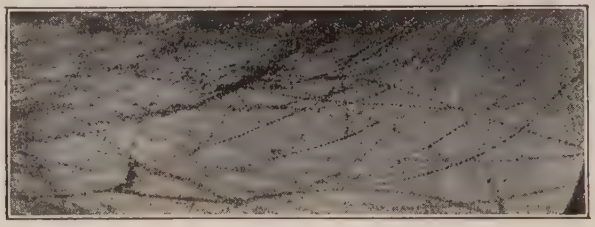
Asterionella before (*A*) and after (*B*) treatment with copper sulfate, 1/5 p.p.m. Note effect upon coloring matter. Magnification 150. Causes geranium to fishy odor.



Water concentrate as it appears under the microscope. 1. *Synedra*, fine tooth comb. 2. *Synedra*, needle-form. 3. *Asterionella*. 4. *Melosira*.



Fragilaria, magnification 150.



Ulothrix, magnification 75.

Identification of Forms.—On page 2106 is shown a section from a page of the record book used in New York City's Water Department Laboratories, showing the classification of organisms and the commoner forms found.

As the magnification used for counting is only 87 one must learn to identify the forms quickly at that magnification. Occasionally it is necessary to use the one-half-inch ocular to make certain the identification, the latter magnification being 146. Young forms frequently differ from mature forms and confusion arises. It may be helpful to mention certain distinguishing features for some of these commoner forms, avoiding so far as possible technical terms.

Asterionella (little star) in its usual form is readily recognized. Four to eight arms connected at one end, slightly larger than the other end, and radiating from the attached ends suggest its name. The arms are usually more slender near the center in girdle view. The coloring matter appears as regularly spaced dots or dashes strung along the arm in single row. There is another form of *Asterionella* in which the arms attach at either end in zig-zag manner with occasionally four arms arranged in star fashion. This form may be confused with "*Diatoma*" or "*Tabellaria*," but may be distinguished by the appearance of individual arms in valve view, *Diatoma* having cross striations and *Tabellaria* an oval outlined in a swollen center.

It may be mentioned that Diatoms have two valves fitting together like clams, oysters or scallops but different in that they overlap like the cover and bottom of a petri dish or a pill box. The valve view is that of the top of the box and girdle view that of the edge. (Different authors use different terms. The above is according to Whipple.)

Diatoma in girdle view has straight sides and square ends, joining at the corners to form zig-zag chains. The valve view is distinctive from *Asterionella* and from *Tabellaria*; it has cross striations.

Tabellaria usually has wider arms than *Asterionella* or *Diatoma* and two well-defined parallel marks or lines extending from each end nearly to the middle. In some forms these are missing. The arms join in zig-zag fashion with sometimes three or four in star shape. As mentioned before the valve view is distinctive, being swollen and marked with an oval at the center. There is also a distinctive short chubby form.

Synedra in common form looks like a fine-tooth comb, the needle-like individuals being attached side by side at the center forming a serrated edge. The edge distinguishes it from *Fragilaria* which also forms masses side by side but the ends of the latter are square with no appearance of teeth. Frequently *Synedra* exists only in individual short needles and again in very long needles.

Meridion also joins side by side but being wider at one end than the other forms disc-like patterns. The valve view is also distinctive, like a base-ball club and striated cross-wise.

Gomphonema is also wedge-shaped like *Meridion* but does not join in masses and in valve view is shaped like a rolling pin. It has a pedicle which is frequently missing.

Many forms, once seen, are very readily distinguished, *Stauroneis* like an elongated diamond with a cross marked from corner to corner, *Pleurosigma*, with a double curve reminding one slightly of the letter "S," *Navicula*, shaped like a little boat, *Melosira*, with its cylindrical cells joined end to end to form filaments containing considerable coloring matter. *Cyclotella* appears usually

as small perfect circles without contents whereas *Stephanodiscus* is a larger circle with coloring matter conspicuous and sometimes concentric markings visible on the circumference. On edge a view as of a pill box is often obtainable.

The coloring matter of the Diatoms may appear from yellow to brown but often a mere black and white effect without much suggestion of color.

The Chlorophyceae (green growth) have green coloring matter. The common forms are readily distinguished and remembered from illustrations. *Dictyosphaerium* and *Dimorphococcus* are similar small coccus-like forms joined by spider-like threads together, the former from a concave side, the latter from a convex side. *Pandorina* and *Eudorina* are coccus-like forms set in a jelly ball, the former with the coccus bodies grouped together closely at the center, the latter with them separated and spaced regularly near the surface. *Volvox* is a large revolving jelly-like hollow ball with the surface dotted with coccus forms and similar to *Uroglena* of the Protozoa, but differs in containing several conspicuous larger green cells which are in reality young *Volvoces*.

The Cyanophyceae (blue growth) contain a blue-green coloring matter. *Anabaena* appears like a string of beads. It differs from Nostoc in not having a gelatinous sheath, from *Sphaerozyga* in that its spores and heterocysts are not adjacent whereas in the latter a heterocyst is between two spores. The spores are larger than the vegetative cells. It differs from *Cylindrospermum* in that the latter has its heterocysts terminal with large spore adjacent, and the latter filament is sometimes tapering.

Aphanizomenon under high power has a beaded appearance and contains a very long oval spore which is scarce. Under the ordinary power *Aphanizomenon* appears like a pencil mark on drawing paper and frequently appears in attached masses of filaments.

Oscillaria is a pale blueish filament of even color without granulation, with rounded ends, straight sides (i.e., no beaded appearance) and cross striations. At times it may be seen to oscillate or wave back and forth (hence its name).

Of the Schizomycetes, *Crenothrix* is fairly common and occurs in well waters containing iron or manganese. It occurs as dark brown masses due to discoloration with iron or manganese. The latter may be dissolved by acid when the oblong cells become visible embedded in a gelatinous sheath, but not touching each other, and forming a filament. *Anthophysa* pedicles, a Protozoon, are sometimes mistaken for it but the latter is usually branched like a "Y" and has longitudinal striations. The colonies resemble *Synura*, but are colorless and generally smaller.

The Protozoa are the lowest forms of animal life, unicellular in structure, though they may aggregate in colonies. Of *Dinobryon* frequently only the pencil-like outlines of the tiny cups or trumpet-like shells are visible (and difficultly seen), one set in another, to form branching aggregations. The spores of *Dinobryon* are sometimes mistaken for *Cyclotella*. *Glenodinium* and *Peridinium* are oval and each has a groove across the center. The former is smaller and has a smoother outline than the latter. *Synura* is a small moving yellowish ball of oval animalcules joined concentrically and closely packed. *Uroglena* is a large jelly-like hollow ball of minute animalcules, the latter embedded near the surface, similar in appearance to *Volvox*, as previously mentioned, but lacking the large green cells. It rolls around slowly in the center of the liquid of the cell. Broken pieces have the shape of a piece of a

rubber ball. It is visible to the naked eye and recognizable in the bottle.

Rotifera, Crustacea, etc. (more complicated animal forms) are readily distinguished from their pictures in most instances. Many are visible to the naked eye. *Cyclops* may readily be recognized in the bottle by its shape and swift darting motion. It appears about the size of a pin head shaped somewhat like a tiny fish, but wider in proportion. *Bosmina* (little cow) and *Acarina* (little spider) each has a peculiar characteristic jerky motion.

CONTROL OF MICROSCOPIC ORGANISMS

Troublesome microscopic growths are controlled as follows: Reservoirs are shut off from the service and bypassed until the forms die out under storage which may take three weeks to three months. Aeration by fountains will disintegrate certain fragile forms like *Uroglena*, *Anabaena*, even *Asterionella*, and assist in removing odors. *Crenothrix* may be controlled by chloramine or liquid chlorine (Monfort & Barnes). Liquid chlorine has also been widely employed the last 16 years to help control *Synura*, *Uroglena*, *Dinobryon* etc. But the method of widest application is that of Moore & Kellerman, the application of copper sulfate in dosage ranging from .05 to 1.00 part per million by weight according to the particular genera of microscopic organisms present. The chemical has been usually applied by rowing around in boats dragging burlap bags, containing, usually, fifty pounds each, through the surface of the water, allowing wind, wave and diffusion to mix the treated water with the remainder. On large reservoirs launches are employed with arrangement on either side for suspending the copper sulfate crystals in the water and the action of the propeller causes considerably wider distribution of the chemical. In the last few years special methods of distribution by launch have been devised, particularly on the west coast, the crystals being distributed in solid form by a mechanical blower by one method and by pumped water by another method. These methods are said to accomplish wider, more uniform, and faster distribution. Better depth effect is also accomplished, the crystals dissolving as they sink. Size of crystal is also chosen depending upon depth to be treated.

New York City has demonstrated, very satisfactorily, that dry feed of the chemical by automatic accurate electrical apparatus to the water flowing in an aqueduct a short time before entering the reservoir is absolutely feasible and successful even at winter temperatures and with ice-covered reservoirs. The feed is by means of a slowly moving shutter fed from a hopper. The copper sulfate drops into floating perforated wooden box in a narrowed portion of the aqueduct. Dosage is similar to that used in the reservoirs by the boat method, and under such circumstances the killing dosage is known exactly.

The effect of treatment of microscopic organisms by copper sulfate is shown by an immediate intensification of distinctive odors, by reduction of the number of organisms in the water through sedimentation, by the appearance of

the organisms under the microscope—the coloring matter being knocked to pieces, so to speak. Sometimes there is an increase in the water bacteria which feed upon the decayed organisms. The Cyanophyceae may produce scum after treatment which is of varied colors, pale blue, yellow, red or brown.

Sometimes fish are killed by the treatment but this is more apt to occur from smothering due to clogging of the gills with dead organisms or reduction of oxygen by the dead organisms. It is only occasionally that fish are killed in quantities, even though larger doses are usually applied than shown in the following table calculated from data published by Moore & Kellerman:

Limiting Dosage of Copper Sulfate for Fish Life

Fish	Parts per Million	Pounds per Million Gallons (Approximate)
Trout	0.14	1.2
Carp	0.33	2.8
Suckers	0.33	2.8
Catfish	0.40	3.5
Pickerel	0.40	3.5
Goldfish	0.50	4.2
Perch	0.67	5.5
Sunfish	1.33	11.1
Black Bass	2.00	16.6

Experience differs with waters of different composition and with temperature as to the right dosage to apply for each organism. It is believed that it is a waste of copper sulfate to apply an insufficient quantity. When the correct quantity is applied the water is usually cleared within three to four days. The following table on pages 2113–2114 is made up from data furnished by Moore & Kellerman, Whipple, various other sources and personal experience. The latter are starred. Results in recent years with chlorine are also included.

The following illustration shows the corner of a bacteriological laboratory for the microscopical examination of water.

Fig. 294.—Microscopical Apparatus, Catskill Laboratory, Ashokan, N. Y.

Chemicals Required for Treatment of Different Genera

Organisms	Odor	Parts per Million	Pounds per Mil. Gals.	Chlorine p.p.m.
DIATOMACEAE:				
Asterionella ‡	Aromatic, geranium, fishy	0.12*–0.20*	1.0–1.7	0.5*–1.0*
Cyclotella †‡	Faintly aromatic	.....	....	1.0
Diatoma †	Faintly aromatic	.....	....	
Fragilaria †		0.25	2.1	
Melosira †‡§		0.2	1.7	2.0
Meridion	Aromatic	.....	....	
Navicula †		0.07	0.6	
Nitzchia §		0.50	4.2	
Synedra †‡	Earthy	0.36*–0.50*	3.0–4.2	1.0
Stephanodiscus		0.33	2.8	
Tabellaria ‡	Aromatic, geranium, fishy	0.12*–0.50*	1.0–4.2	0.5*–1.0
CHLOROPHYCEAE:				
Cladophora †		0.50	4.2	
Closterium		0.17	1.4	
Coelastrum †		0.05–0.33	0.4–2.8	
Conferva †		0.25	2.1	
Desmidium		2.00	16.6	
Dictyosphaerium ‡	Grassy, nasturtium, fishy	.....	....	0.5*–1.0
Draparnaldia		0.33	2.8	
Eudorina	Faintly fishy	2.0–10.00	16.6–83.0	
Entomophora		0.50	4.2	
Gloeocystis	Offensive	.....	....	
Hydrodictyon	Very offensive	0.10	0.8	
Microspora		0.40	3.3	
Palmella		2.00	16.6	
Pandorina	Faintly fishy	2.0–10.00	16.6–83.0	1.0
Protococcus		.....	....	
Raphidium		1.00	8.3	
Scenedesmus		1.00*	8.3	
Spirogyra †		0.12	1.0	0.7–1.5
Staurastrum	Grassy	1.50	12.5	
Tetrastrum		.....	....	1.0
Ulothrix		0.20*	1.7	
Volvox ‡	Fishy	0.25	2.1	0.3*–1.0
Zygnema		0.50	4.2	
CYANOPHYCEAE:				
Anabaena ‡	Moldy, grassy, vile	0.12*–0.48	1.0–4.0	0.5*–1.0
Aphanizomenon ‡	Moldy, grassy, vile	0.12*–0.50*	1.0–4.2	0.5*–1.0*
Clathrocystis	Sweet grassy, vile	0.12*–0.25*	1.0–2.1	0.5*–1.0
Coelosphaerium ‡	Sweet grassy	0.20*–0.33	1.7–2.8	0.5*–1.0
Cylindrospermum	Grassy	0.12	1.0	
Microcystis		0.20	1.7	
Oscillaria †		0.20–0.50*	1.7–4.2	1.1
Rivularia	Moldy, grassy	.....	....	

The organisms where odors are expressed have been in sufficient quantity at one time or another to cause the characteristic odor.

* Dosage successful in New York City's supplies.

† These organisms have caused trouble other than odor.

‡ These organisms have been affected by chlorine producing characteristic odor and in many cases controlled by dosage ranging from 0.3 to 3 p.p.m. depending largely on amount of organisms.

§ Controlled by excess caustic lime, 5 p.p.m. in the case of the diatoms.

NOTE.—Range of dosage largely due to temperature.

Chemicals Required for Treatment of Different Genera (*Continued*)

Organisms	Odor	Parts per Million	Pounds per Mil. Gals.	Chlorine p.p.m.
PROTOZOA:				
Bursaria	Irish moss, salt marsh, fishy	.....	....	
Ceratium †‡	Fishy, vile (rusty brown color)	0.24*–0.33	2.0*–2.8	0.3*–1.0
Chlamydomonas		0.50–1.0	4.2–8.3	
Cryptomonas	Candied violets	0.50	4.2	
Dinobryon ‡	Aromatic, violets, fishy	0.18*	1.5	0.3*–1.0
Endamoeba histolytica (cysts)				25.0–100.0
Euglena		0.50	4.2	
Glenodinium	Fishy	0.50*	4.2	
Mallomonas	Aromatic, violets, fishy	0.50	4.2	
Peridinium	Fishy, like clam-shells	0.50*–2.00	4.2–16.6	
Synura ‡	Cucumber, muskmelon, fishy, bitter taste	0.12*–0.25*	1.0–2.1	0.3*–1.0
Uroglena ‡	Fishy, oily, cod liver oil	0.05*–0.20*	0.4–1.6	0.3*–1.0
CRUSTACEA:				
Cyclops †‡§		.....	....	1.0–3.0
Daphnia †‡§		2.0	16.6	1.0–3.0
SCHIZOMYCETES:				
Beggiatoa †	Very offensive decayed	5.00	41.5	
Cladothrix		0.20	1.7	
Crenothrix †‡	Very offensive decayed, medicinal with chlorine	0.33–0.5*	2.8–4.2	0.5*
Leptothrix †		.....	....	
Sphaerotilis, natans	Very offensive decayed	0.40	3.3	
Spirophyllum †		.....	....	0.25*
Thiothrix †‡	Very offensive decayed	.....	....	0.5*–1.0
FUNGUS:				
Achlya		.....	....	0.6*
Leptomitus		0.40	3.3	
Saprolegnia †		0.18	1.5	
MISCELLANEOUS:				
Chara †		0.10–0.50	0.8–4.2	
Nitella, flexilis †	Objectionable	0.10–0.18*	0.8–1.5	
Potamogeton †		0.30–0.80	2.5–6.7	
Nais †		.....	....	1.0*
Blood worm, chironomus †		....	....	15.0–50.0
Blood worm, gnats		.....	....	3.0

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BACTERIOLOGICAL EXAMINATION OF WATER

The routine bacteriological examination is essentially simple. It consists of obtaining empirically the total number of bacteria under certain standard conditions and of testing for the intestinal group, *B. coli*. Usually only under special conditions is search made for specific disease bacteria which may be carried by water supply, such as *Bacillus typhi*, *Bacillus paratyphi*—A and B, *Spirillum cholerae*, *Bacillus dysenteriae*—various types, *Bacillus anthracis*, etc.

SAMPLING

Samples must be taken in dry-sterilized bottles, with well-ground glass stoppers. Two ounce capacity is usually sufficient for routine tests. The bottles are preferably protected by covering the stoppers and necks with tinfoil and further protected by placing in a metal screw-top can (two inch by four inch). It is frequently convenient to use quart bottles steam-sterilized at fifteen pounds pressure, and capped with tinfoil, when special samples are to be brought in by hand,—the same sample serving for the physical, microscopical and chemical analyses after making the bacteriological examination. Such samples transported in leather bags of proper size do not change temperature more than a few degrees in several hours on the hottest days though not protected by ice. For the two-ounce bottles special aluminum cases, holding small quantities of ice and fitting the bags, are light and convenient. For shipping, the small bottles may be packed in a copper-lined wooden box containing a receptacle for the bottles and space for ice below. (See Fig. 295.)

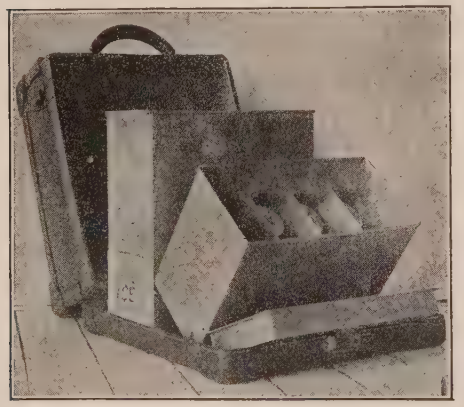


Fig. 295.—Collection Apparatus for Bacteriological Samples.

In sampling care must be taken to take representative samples, avoiding contamination and avoiding stagnant water. Temperature is often a guide but it must be taken from the source or in a separate bottle with the thermometer

bulb immersed in the water a few minutes before reading. Allow tap samples to run thoroughly, particularly in warm boiler rooms. Handle sterilized bottles by the bottom and keep fingers away from the necks. Handle stoppers with the tinfoil in place. Avoid splashing or over-running bottles. In streams plunge bottle below the surface and sample by swinging hand up-stream with mouth of bottle pointed up-stream so as to avoid water washing over the hand into bottle. Similarly in a reservoir, swing the mouth of the bottle forward while filling. Do not rinse a sterilized bottle. These rather minute directions are given because in a long experience they have frequently been found necessary. Experts do not always take the samples though the value of their work depends upon the care with which the samples are taken. Men have even been caught reading thermometers after drawing them up twenty feet from the surface of a reservoir.

Samples from a depth in a reservoir are best taken if possible from an effluent pipe when regular draft is from a depth. In other cases sterilized bottles may be lowered to the required depth and stoppers pulled out by means of special samplers. In many cases it has been found satisfactory to take them by the two-bottle method as used for dissolved oxygen and described under "Microscopic Examination of Water." In this case the quart bottle should be thoroughly cleaned, handled as little as possible, and the water poured into a bacteria bottle after drawing to the surface. The quart bottle is pretty thoroughly rinsed during the process of sampling. (Fig. 291, p. 2102.)

Samples should be tested the same day they are collected, preferably within a few hours. Expressed and iced samples will probably give a fairly reliable index of *B. coli* content but cannot be relied on for total counts.

Apparatus and Materials Needed

Bacteria bottles—two-ounce glass-stoppered (well ground).
Metallic containers for above, screw-cap, two inch by four inch.
Tinfoil, five inch wide, in rolls for capping.
Bacteria certificates for sample data.
Containers for carrying samples—leather bags with aluminum ice cases to fit.
Containers for shipping samples—copper-lined ice chests.
Dry-sterilizer for bottles and pipettes, to operate at 170° C.
Autoclave to operate at 15 pounds steam pressure, sterilization of media.
1 ml. pipettes with two marks and also conveniently graduated to show 0.1 ml. above the upper 1 ml. mark.
10 ml. pipettes, preferably straight tube pipettes with graduation also for 5 ml. and 9 ml.
Pipette boxes for sterilized pipettes, $3\frac{1}{4}''$ square by $14''$ long.
Dilution test tubes, $1''$ diameter, medium weight.
Media test tubes, $\frac{5}{8}''$ diameter, heavy weight, not lipped.
Dilution flasks, Erlenmeyer, 16-ounce capacity, for sterilized water.
Flasks, $\frac{1}{2}$ liter, 1 liter, etc., for media preparation and bulk storage.
Test tube racks for dilution tubes.
Wire cages for media tubes, $4''$ by $5''$ by $5\frac{1}{2}''$ high.
Non-absorbent cotton for plugging tubes.
Footless Smith tubes for *B. coli* tests, or small test tubes inverted in large test

tubes for same, capacity in either case four times the amount of water to be tested.
Metal racks for Smith tubes.
Agateware double boilers for making media.
Agateware kettles for making media.
Agateware funnels, 6 inch, for filtering media.
Cotton flannel for filtering media.
Large beakers for making media.
Earthenware pitchers for filling tubes with media.
Side-neck burettes for filling tubes with media (side neck connected to funnel of media).
Apparatus for keeping media warm while filtering.
Gas stoves for heating media.

Fig. 296.—Bacteriological Apparatus. Fermentation Tubes, Petri Dishes, Culture Media, etc.

Petri dishes, 10 cm. diameter and flat bottomed, with both glass covers (20° C. incubation) and porous covers (37° C. incubation).
Agateware sauce pans for melting media in tubes before planting.
20° C. incubator with thermometer, automatic regulator and safety burner.
37° C. incubator with thermometer, automatic regulator and safety burner. (In many laboratories the incubators are now electrically operated.)
Burner for flaming tubes before planting.
Counting stand with engraved lines to assist in counting.
Engraver's lens for counting, B. & L. 146, magnification $2\frac{1}{2}$ diameters, $3\frac{1}{2}$ X.
Tallying register for counting.
Balance, similar to an apothecary's, for quick weighing.
Balance, analytical beam type, for accurate weighing.
Record books for bacteriological results.
Microscope with condenser and assortment of lenses: at least $\frac{1}{4}''$, $\frac{1}{2}''$ and $1''$ eyepieces and $\frac{2}{3}''$, $\frac{1}{6}''$ and $1/12''$ objectives. (Satisfactory hanging drops

may be made with $\frac{1}{2}''$ eyepiece and $\frac{1}{6}''$ objective. The 1/12″ is used only in oil immersion with condenser.)

Slides, plain and concaved (latter for hanging drops).

Cover slips, round or square.

Platinum needles with holders for transferring cultures.

Cleaning mixture for cleaning glassware.

Distilled water for preparation of all culture media and reagents.

Meat extract; Digestive Ferments Company's Bacto Beef Extract is satisfactory.

Peptone: N. Y. City Water Department Laboratories have found Digestive Ferments Company's reliable. (Some laboratories have found Armour's and Fairchild's satisfactory.)

Lactose and other sugars the purest obtainable.

Agar. Frequently needs soaking in water and draining before use because of salt. Shall be dried $\frac{1}{2}$ hour at 105° C. before weighing.

Gelatine, of light color, containing not more than a trace of arsenic, copper, sulfides, free from preservatives, and of such a melting point that "standard nutrient gelatin" shall not melt below 25° C. Gelatin shall be dried $\frac{1}{2}$ hour at 105° C. before weighing.

Litmus—reagent litmus of highest purity (not litmus cubes) or azolitmin (Kahlbaum's).

Certified Dyes—Basic fuchsin, Eosin yellowish, Methylene blue, Brilliant green.

General chemicals—chemically pure so far as possible.

Hellige comparator for hydrogen-ion with color discs for brown-thymol-blue, and cresol red and phenol red.

Adjustment of Reaction.—The final reaction for broth, gelatin and agar shall be between pH 6.4–7.0. For Endo medium the final reaction after the addition of chemicals should be pH 7.8–8.2. The eosin methylene-blue agar does not require adjustment. The increase in the hydrogen-ion concentration during sterilization will vary slightly with the individual sterilizer in use and the initial reaction required in order to obtain the correct final reaction will have to be determined.

The simplest method is the use of the Hellige Comparator which employs discs with colored glasses. Each disc contains the range of colors for a single dye, 0.2 pH apart, and the colors are a very good match and accurate. Brom-thymol-blue has a range 6.0–7.6, Phenol Red 6.8–8.4, and Cresol-red a range 7.2–8.8. The first covers all the ordinary media, the second Brilliant-green bile diluted, and the latter covers Endo. Procure the dyes from any of the firms supplying it for pH determination. The preparation of the dye solutions is as follows according to Clark. Rub up a decigram of brom-thymol blue in 3.2 ml. of N/20 sodium hydroxide. Dilute to 25 ml. with distilled water, making 0.4% solution. Dilute again for use to 0.04% solution. Rub up a decigram of Cresol-red in 5.3 ml. of N/20 sodium hydroxide. Dilute to 25 ml. with distilled water, making 0.4% solution. Dilute again for use to 0.02% solution. With Phenol-red 5.7 ml. of N/20 sodium hydroxide is used and final solution is .01% strength. In testing bacteriological media, for example agar, add to 8 ml. of distilled water 2 ml. of melted agar, add $\frac{1}{2}$ ml. of the brom-thymol-blue solution, mix by pouring into one of the comparison tubes. In another comparison tube pour the similarly diluted media but without the dye and place this behind the colored glasses. Comparison should be made at once and is

sufficiently accurate. The prepared solutions of the dyes gradually change in pH. The solution should be sterilized and stored in sterile pyrex bottles. Sterile pipettes should also be used. Always allow the dye to drain from the pipette and never blow out as the carbonic acid of the breath will influence results. In laboratories which can afford to have the equipment, the dye solutions should be checked by the electrometric method and proper corrections applied. For this purpose standard buffer solutions covering a range of pH should be purchased.

Sterilization.—All media and dilution water shall be sterilized in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs. All air must be forced out of the autoclave before the pressure is allowed to rise. As soon as possible after sterilization the media shall be removed from the autoclave and cooled rapidly. Rapid and immediate cooling of gelatin and lactose broth is imperative.

Media shall be sterilized in small containers, and these must not be closely packed together. No part of the medium shall be more than 2.5 cm. from the outside surface of the glass. All glassware shall be sterilized in the dry oven at 170° C. for at least 1 hour. Sample bottles may be sterilized in a steam autoclave at 15 lbs. pressure for $\frac{1}{2}$ hr.

Nutrient Broth.—To make one liter:

1. Add 3 grams of beef extract and 5 grams of peptone to 1000 ml. of distilled water.
2. Heat slowly on a steam bath to at least 65° C., stirring until dissolved.
3. Make up lost weight with distilled water and adjust the reaction so that final pH will be between 6.4 and 7.0 after sterilization.
4. Bring to a boil over a free flame. Cool to 25° C. and filter through filter paper until clear.
5. Distribute in test-tubes, 10 ml. to each tube.
6. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs.

Sugar Broths.—Sugar broths shall be prepared in the same general manner as nutrient broth with the addition of 0.5% of the required carbohydrate just before sterilization. The removal of muscle sugar is unnecessary as the beef extract and peptone are free from any fermentable carbohydrates. The reaction of sugar broths shall be pH 6.4–7.0. Sterilization shall be in the autoclave at 15 pounds (120° C.) for 15 minutes after the pressure reaches 15 pounds, provided the total time of exposure to heat is not more than one-half hour; otherwise a 10% solution of the required carbohydrates shall be made in distilled water and sterilized at 100° C. for $1\frac{1}{2}$ hours, and this solution shall be added to sterile nutrient broth in amount sufficient to make a 0.5% solution of the carbohydrate and the mixture shall then be tubed and sterilized at 100° C. for 30 minutes, or it is permissible to add by means of a sterile pipette directly to a tube of sterile neutral broth enough of the carbohydrate to make the required 0.5%. The tubes so made shall be incubated at 37° C. for 24 hours as a test for sterility.

Nutrient Gelatin.—To make one liter:

1. Add 3 grams of beef extract and 5 grams of peptone to 1000 ml. of distilled water and add 100 grams of gelatin dried for one-half hour at 105° C. before weighing.

2. Heat slowly on a steam bath to 65° C. until all ingredients are dissolved.

3. Make up lost weight with distilled water and adjust the reaction so that final pH shall be 6.4–7.0.

4. Bring to boil. Filter through cloth and cotton until clear.

5. Distribute in test-tubes, 10 ml. to each tube, or in larger containers as desired.

6. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs. Cool rapidly as soon as possible.

Nutrient Agar.—To make one liter:

1. Add 3 grams of beef extract, 5 grams of peptone and 12 grams of agar, dried for one-half hour at 105° C. before weighing, to 1000 ml. of distilled water. Boil over a water bath until all the agar is dissolved.

2. Make up lost weight with hot distilled water and adjust the reaction so that final pH shall be 6.4–7.0.

3. Filter through cloth and cotton until clear.

4. Distribute in test-tubes, 10 ml. to each tube, or in larger containers, as desired.

5. Sterilize in the autoclave at 15 lbs. (120° C.) for 15 minutes after the pressure reaches 15 lbs.

Note.—The Water Department Laboratories of New York City for many years have used and found the following method of clarifying agar very efficient: The prepared agar is placed in a suitable container and filtered upward by vacuum in a pressure cooker into four one-quart jars. The mouth of the jar is covered with a filter made of a thick wad of absorbent cotton 2 inches thick between two layers of cotton flannel, the filter occupying the neck of the jar. The cotton flannel is tied securely in place on the outside of the neck. These jars are inverted in the container holding the agar and placed in the pressure cooker. The pressure is brought up to 15 pounds and allowed to cool. Upward filtration takes place under vacuum.

Eosin Methylene Blue Agar

1. To 1000 ml. distilled water add 10 grams of peptone, 2 grams of dipotassiumphosphate (K_2HPO_4) and 15 grams of undried agar. Boil ingredients until dissolved and make up any loss due to evaporation with distilled water.

2. Place measured quantities (100 or 200 ml.) in flasks or bottles and sterilize in the autoclave at 15 pounds for 15 minutes.

3. Just prior to using, melt above agar in a water bath and add the following to each 100 ml. of agar:

lactose, sterile 20% solution 5 ml.
eosin, yellowish, 2% aqueous solution 2 ml.
methylene blue, 0.5% aqueous solution 2 ml.

4. Mix thoroughly and pour medium into Petri dishes, allow to harden and inoculate by streaking on the surface.

Endo Medium

Formula I

1. **Preparation of Stock Agar.**—Add 5 grams of beef extract, 10 grams of peptone and 30 grams of undried agar to 1000 ml. of distilled water.

Boil until the agar is dissolved and make up lost weight with distilled water.

Adjust the reaction so that the pH reading after sterilization will be 7.4. Clarify if desired. Add 10 grams of lactose and dissolve.

Place in small flasks or bottles, 100 ml. to each, and sterilize in autoclave at 15 lbs. pressure for 15 minutes after the pressure has reached 15 lbs.

2. **Preparation of Plates.**—Prepare a 3% solution of certified basic fuchsin in 95% methyl alcohol. Allow to stand 24 hours and filter.

Melt lactose agar as prepared above and to each 100 ml. add 1 ml. of the 3% basic fuchsin solution and 0.125 gram of anhydrous sodium sulfite dissolved in 5 ml. of distilled water. The sulfite solution must be freshly prepared. Mix thoroughly, pour plates with usual precautions against contamination and allow to harden.

The medium should be light pink when hot and almost colorless when cool. If the medium is too highly colored before incubation the strength of the basic fuchsin solution may be varied.

FORMULA II

Dipotassium phosphate	3.5 grams
Bacto peptone	10.0 "
Agar (washed and dried)	15.0 "
Water (distilled)	1 liter
Lactose (c.p.)	10.0 grams

To each 100 ml. of the above add:

Sodium sulfite (Anhydrous)	0.25 "
Basic fuchsin filtered 10% alcoholic solution	0.5 ml.

NOTE.—It is difficult to make a 10% solution with some basic fuchsin preparations.

Brilliant-Green Lactose Peptone Bile.—The composition for approximately one liter is as follows:

Dissolve 10 grams of peptone and 10 grams of lactose in not more than 500 ml. of distilled water.

Add 200 ml. of fresh ox bile or 20 grams of dehydrated ox bile dissolved in 200 ml. of distilled water. The solution of dehydrated ox bile shall have a pH between 7.0 and 7.5.

Make up with distilled water to approximately 975 ml. and adjust reaction to 7.4 pH.

Add 13.3 ml. of a 0.1% solution of Brilliant-Green in distilled water and add sufficient distilled water to make the volume 1000 ml. Filter through cotton, distribute in fermentation tubes and sterilize at 15 lbs. pressure for 15 minutes after pressure reaches 15 lbs. Total exposure to heat should not exceed one-half hour. Cool rapidly after removal from autoclave.

The reaction after sterilization should be between pH 7.1 and 7.4.[6]

Brilliant-Green Lactose Peptone Bile of the above formula may be obtained mixed in dry form from the Digestive Ferments Company, Detroit, Mich., and has the following composition:

Dried oxbile	20	grams
Peptone	10	"
Lactose	10	"
Brilliant-Green	0.0133	"

[6] The pH may be determined colorimetrically with Hellige equipment by use of Phenol Red indicator in 0.01% solution using dilution of medium of 1 : 4. Results check with those determined potentiometrically. The color of the medium is compensated by the equipment.

For a water inoculum of 1 ml. or less or for loop inoculations the above dry material should be used in proportion of 4 grams to 100 ml. media water (distilled) and tubed in 10 ml. quantities. The concentration of bile in the inoculated tube will then be 2% and of Brilliant-Green 1 part in 75,000. For 10 ml. water samples a total volume of water plus medium of 30 ml. is used and the medium is made using 6 grams of the above dry mixture per 100 ml. of media water, which results in the same final density of ingredients.

For routine presumptive planting on a large scale it is simpler to make up double strength media as follows:

Dissolve in 4 liters of hot distilled water, 160 grams of dessicated bile, 80 grams of peptone, and add 15 ml. of N/1 sodium hydroxide. Remove from flame and add 80 grams of lactose. After solution filter through flannel, make up to original volume and add 10.6 ml. of 1% Brilliant-Green.

For small tubes in which are planted 1 ml. or less of water, dilute 1500 ml. of the above to 3000 ml. and tube in 10 ml. quantities.

For large tubes in which are planted 10 ml. of water, dilute 2500 ml. to 3750 ml. and tube in 30 ml. quantities.

For testing of 100 ml. quantities of water use the double strength media as prepared, 100 ml. quantities of media per 100 ml. quantity of water tested.

Hesse Agar.—The composition for approximately 1 liter is as follows:

Agar (dried)	4.5 grams
Peptone	10. "
Beef extract, Liebig's	5. "
Salt (sodium chloride)	8.5 "
Distilled water	1000. "

Dissolve 4.5 grams of dry agar in 500 ml. distilled water by heating over a free flame, making up loss in weight by evaporation. Into another vessel 500 ml. of distilled water is poured and to this is added 10 grams of peptone, 5 grams of Liebig's beef extract, and 8.5 grams of salt. This is heated until all is dissolved and the loss in weight by evaporation is made up by adding distilled water.

Add the two solutions together; boil 30 minutes; make up loss in weight with distilled water, filter through absorbent cotton held in the funnel by cotton flannel, passing the filtrate through several times until perfectly clear. Test the reaction; adjust, if necessary, to pH = 7.0, and tube, using 10 ml. in each tube. Sterilize for 15 minutes at 15 lbs. pressure in an autoclave. Cool with running tap water and store in an ice-chest, the air of which is saturated with moisture.

Russell Media.—To ordinary extract agar adjusted neutral to litmus add 1% of lactose and 0.1% of glucose and sufficient litmus to give a good color. Tube and slant leaving a generous "butt" at bottom of tube for stab inoculation.

EXAMINATION OF WATER FOR TOTAL BACTERIA

The gelatine count is more particularly useful in connection with determining the efficiency of filter plants, since the counts are higher than the agar counts (averaging usually about ten times as high) and in examination of well waters by indication of surface contamination through the presence of liquifiers.

In plating with gelatine media it is usually necessary to use 0.1 ml., or less, as well as 1 ml., in order to obtain the right amount of colonies on a plate. Standard methods require planting in duplicate.

Melt tubes of nutrient gelatine or nutrient agar in boiling water,—the latter needs thorough boiling for several minutes to soften entirely. Let cool until luke-warm, just barely warm to the touch. Shake the sample of water vigorously and introduce 1 ml. or less into the bottom of a petri-dish lifting the cover on one side but not removing from over the bottom. The quantity of water used should of course be accurately measured. Be careful not to contaminate the pipette by touching to anything other than the inside bottom of the petri-dish. Use glass-covered petri-dishes for incubation at 20° C. and porous covers for 37° C., in order to overcome spreaders at the higher temperature. Remove a tube of the media from the warm water, dry with a towel, remove the cotton plug, flame the open end of tube and pour into petri-dish. Carefully rotate dish to mix the media with the water and set on a level plate to harden. Agar hardens so quickly that it must be handled and mixed expeditiously. Incubate gelatine plates at 20° C. and agar plates at 37° C.

The gelatine plates are counted after 48 hours and the agar plates after 24 hours.

Each minute bacillus must grow where caught in the solid medium and after sufficient time forms a colony large enough to be seen with the naked eye. Many are however very tiny, so that a hand lens magnifying two and one-half diameters is used in counting. A tallying machine is used to keep count, one tally being made for every three colonies usually, to assist the speed of counting. For accuracy there should be 30 to 300 colonies on a plate, unless less than 30 grew from 1 ml. Fictitious accuracy should be avoided. The following table should be followed in recording results:

Number of bacteria per ml.

From	1	to	50	shall	be	recorded	as	found		
"	51	"	100	"	"	"	to	the	nearest	5
"	101	"	250	"	"	"	"	"	"	10
"	251	"	500	"	"	"	"	"	"	25
"	501	"	1,000	"	"	"	"	"	"	50
"	1,001	"	10,000	"	"	"	"	"	"	100
"	10,001	"	50,000	"	"	"	"	"	"	500
"	50,001	"	100,000	"	"	"	"	"	"	1,000
"	100,001	"	500,000	"	"	"	"	"	"	10,000
"	500,001	"	1,000,000	"	"	"	"	"	"	50,000
"	1,000,001	"	10,000,000	"	"	"	"	"	"	100,000

The counting stand is usually marked to facilitate counting, for example, by concentric circles and lines through the center forming sectors. With high numbers four opposite sectors may be counted, situated at right angles to each other, and multiplied by a factor.

Examination for B. Coli

B. coli (bacillus of the colon) represents a group of bacteria inhabiting the large intestines of man and animals. Its presence in water supply signifies possible sewage contamination and the latter means probable typhoid, dysentery, etc., germs. In fact if a drinking water becomes contaminated by sewage, an increase in typhoid fever is almost certain to follow. Animals do not spread typhoid though they may be a factor in paratyphoid. *B. coli* in a water supply may be due to harmless sources and so of little significance.

The present Standard Methods define the coli-areogenes group as including all aerobic and facultative anaerobic Gram-negative non-spore-forming bacilli which ferment lactose with gas formation.

Various classifications of the Coli group have appeared in Standard Methods. The following was included in the 1912 edition. One function of a classification is to make possible a satisfactory identification of distinct members. Numerous members of this grouping were isolated at a hospital from pustules or sores, autogenous vaccine made from each variety isolated, the vaccine used, and the condition cleared up from which the original germ was isolated. For many years pure cultures of these organisms were maintained and their characteristic reactions persisted. This classification therefore appears to have decided usefulness.

Subclassification of B. coli [7]

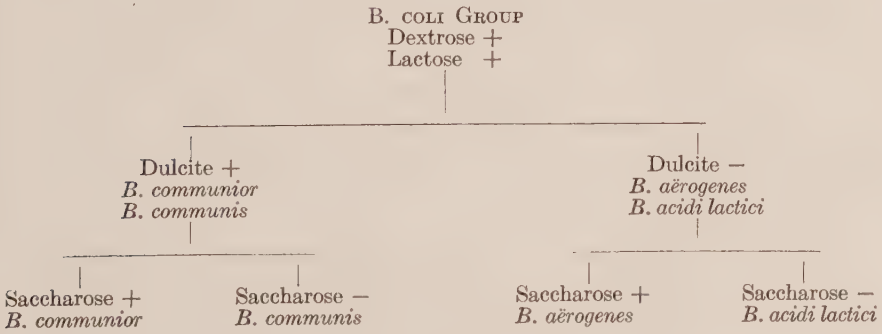
B. coli Group.—The general characteristics common to this group are:

Fermentation of dextrose and lactose with gas formation, short bacillus with rounded ends, non-spore-forming, facultative anaërobe, gives positive test with esculin, grows at 20° C. on gelatine and at 37° C. on agar, non-liquefying in fourteen days on gelatine, gram-staining negative.

The group consists of four species:

B. communior (Durham).
B. communis (Escherich).
B. aërogenes (Escherich).
B. acidilactici (Hüeppe).

This group is differentiated as follows:



[7] Adopted by A. P. H. A., 1912, and recommended by the author.

The "Standard Methods" in testing for the coli-aerogenes group require gas formation in lactose broth plus confirmation in accordance with the following procedure:

"The following classification is included in the 1936 edition of 'Standard Methods.' Its chief usefulness is to divide the group into two broad types, *B. coli* and *B. aerogenes*. The latter type represents members that can persist under adverse conditions, hence less sanitary importance may sometimes be applied to their presence. In England, particularly, more importance is ascribed to the *B. coli* test. Attempt has been made to separate the aerogenes type into Fecal and Non-fecal grouping, but as all types are found in human excrement this separation has not generally been found of any great importance.

Coli-Aerogenes Group—Reaction Classification

Reaction Combinations				Possible Interpretation when Isolated from Water by the Standard Methods		Common Source
Indol	M.R.	V.P.	Citrate	Usually	Occasionally	Applies to Pure Strains Only
+	+	−	−	*Esch. coli*	—	Predominating in feces, about 50% of group in sewage.
−	+	−	−	" "	Non-members of group	Minority in feces.
+	+	−	+	Mixture	Intermediate strains sometimes considered non-typical *E. coli*	Minority in soil and sewage, rarely feces.
−	+	−	+	Intermediate strain	Mixtures or slow-reacting *A. aerogenes*	Soil, minority in sewage and feces.
+	+	+	+	Mixture	Atypical	Soil, sewage.
+	−	−	+	Always mixture		
+	−	+	+	Mixture	*A. cloacae*	Soil, minority in sewage and feces.
−	+	+	+	*A. aerogenes*	Mixture	Majority in soil and on vegetables.
−	−	+	+	" "		Up to 50% of total group in sewage.
−	−	−	+	Extraneous form	*A. aerogenes*	Minority in feces.

"The latest edition of 'Standard Methods,' now sponsored by both the American Public Health Association and the American Water Works Association, has been greatly changed and improved by allowing confirmation of the coli-aerogenes group from gas formation in lactose broth by transplanting to several specific liquid media for confirmation by gas formation. These four media are Brilliant-Green lactose bile, Crystal-Violet lactose broth, Fuchsin lactose broth, and Formate Ricinoleate broth. Confirmation may also be obtained by typical reaction and appearance on Endo agar or Eosin Methylene-Blue agar.

"'Standard Methods' prescribes the following:

"The standard tests for the coli-aerogenes group shall be either the Presumptive, the Confirmed, or the Completed test.

"**Presumptive Test.**—The formation of gas in a standard lactose broth fermentation tube within 24 hours at 37° C. or the formation of gas during a

second 24 hour period with confirmation as described in the next paragraph is presumptive evidence of the presence of members of this group.

" **Confirmed Test.**—The formation of gas within 48 hours at 37° C. in a specified liquid confirmatory medium seeded from a lactose broth tube in which gas is formed, or the appearance of aerobic lactose splitting typical colonies on a specified solid confirmatory medium made from a lactose tube in which gas is formed, confirms the presumption that gas formation was due to the presence of the coli-aerogenes group.

" **Completed Test.**—To complete the demonstration of the presence of this group, it is necessary to show that one or more aerobic plate colonies consist of Gram-negative Non-spore-forming bacilli, which, when inoculated into lactose broth, form gas."

When it is desired to differentiate between the coli and the aerogenes sections of the coli-aerogenes group, the detailed procedure shall not follow primary planting in liquid media, but shall be based upon primary planting in solid media.

Presumptive Test

1. Inoculate a series of lactose broth fermentation tubes with appropriate graduated quantities of the water to be tested. Each tube must contain at least twice as much medium as the portion of sample to be tested.

2. Incubate at 37° C. for 48 hours unless gas appears earlier. Examine each tube at end of 24 hours and, if no gas appears then, again at end of 48 hours. Record presence or absence of gas formation at each examination. More detailed records of amount of gas formed are not necessary for carrying out the standard tests.

3. Formation within 24 hours of gas in the inverted vial in the fermentation tube constitutes a *positive presumptive test.*

4. If no gas or only a small bubble is formed in 24 hours, incubation shall be continued to 48 hours. If gas in any quantity is present after the second but not the first 24 hour incubation period, the test is considered as doubtful and the presence of organisms of the coli-aerogenes group should be confirmed. Confirmed tubes may then be given the same consideration in the presumptive test as those showing gas formation in the first 24 hour period.

5. The absence of gas formation after 48 hours incubation constitutes a negative test (the exclusion of occasional slow gas-forming organisms is considered immaterial).

Confirmed Test

The use of Endo or Eosin Methylene Blue plates or one of the following liquid confirmatory media is permitted: Brilliant-Green lactose bile, Crystal-Violet lactose broth, Fuchsin lactose broth, Formate Ricinoleate broth. The order in which these media are named does not signify their relative values. For confirmation all are equivalent. Selection of any one should depend upon correlation with a series of completed tests.

1. **Endo or Eosin Methylene-Blue Plates.**—Streak one or more plates from a tube showing gas formation in lactose broth from the smallest amount of water tested. It is desirable to make transfers as soon as possible after gas

formation occurs. In order to obtain typical results it is essential that plates be streaked so as to insure presence of some discrete colonies. Transfers should be made not later than the end of the first 24 hour incubation period if gas is formed during this time. If at the end of 48 hours gas is formed in tubes containing less of the sample of water than at 24 hours, transfers should be made from these tubes. (If larger amounts are not transplanted for confirmation, they should be recorded as confirmed, even though the smaller portions may fail subsequently to confirm.)

Incubate the plates at 37° C. for 18 to 24 hours.

If typical colonies develop upon the plates within this period, the confirmed test may be considered positive. If, however, no typical colonies develop within 24 hours, the test cannot be considered definitely negative and the completed test should be made.

2. **Liquid Confirmatory Media.**—Transfer from a lactose broth tube showing gas to the fermentation tube containing the selected confirmatory medium. It is recommended that all lactose broth tubes showing gas be confirmed to comply with this test, but it is allowable to follow the procedure outlined for solid media. Transfers should be made as soon as gas appears. In routine testing it is convenient to make observations and transfers at the end of 24 and 48 hours. In making transfers the tube showing gas shall first be gently shaken or mixed by rotating and the transfer shall be made by means of a wire loop not less than 3 mm. in diameter; or it is permissible to use the sterile capillary tube or sterile pipette when it is considered desirable to transfer larger amounts.

Incubate the inoculated confirmatory tubes for 48 hours at 37° C.

The formation and presence of gas in any amount in the inverted vial in the fermentation tubes at any time within 48 hours constitutes a confirmed test.

Completed Test

Streak one or more Endo or Eosin Methylene-Blue plates from the lactose broth tubes which show gas from the smallest amount of water tested or from the secondary selective medium tubes which show gas. If these plates are streaked from the original lactose broth tubes they should be made at the same time that the secondary selective medium tubes are planted. If plates are used for the confirmed test, completion may be continued after incubation.

Incubate the plates at 37° C. for 18 to 24 hours.

Identification.—From the plates fish one or more typical colonies, or if no typical colonies are present, fish two or more colonies considered most likely to be organisms of the coli aerogenes group, transferring each to an agar slant and a lactose broth fermentation tube. The lactose broth fermentation tubes thus inoculated shall be incubated until gas formation is noted, not to exceed 48 hours. The agar slant shall be incubated at 37° C. for 24 hours, when a microscopic examination for spores and a Gram stain of at least one culture shall be made, selecting when possible the one which corresponds to one of the lactose broth fermentation tubes that has shown gas formation. If none of the lactose broth fermentation tubes contain gas at the end of 24 hours, all agar slants shall be examined, and corresponding tubes examined on the following day.

Results.—The formation of gas in lactose broth and the demonstration

of Gram-negative non-spore-forming bacilli in the agar culture shall be considered a satisfactory completed test.

The absence of gas formation in lactose broth or failure to demonstrate Gram-negative non-spore-forming bacilli in a gas-forming culture constitutes a negative test.

When spore-forming lactose fermenting organisms are found, the culture should be further studied to ascertain the possible presence of the coli aerogenes group with the spore-bearing organism. This may be done by transferring the culture to Formate Ricinoleate broth and incubating 48 hours at 37° C. If no gas is produced only spore-forming lactose fermenters are present. If gas is produced members of the coli-aerogenes group may be present. If gas is produced, the presence of coli-aerogenes organisms should be verified by inoculation of a tube of standard lactose broth and an agar slant. If, after 48 hours, gas is produced in the former and no spores are present in the latter, the test may be deemed "completed." If spores are present, for practical purposes the organisms of the coli-aerogenes group may be considered absent.

Selection of Coli-Aerogenes Tests

The laboratory worker shall be guided by the following basic considerations:

The Completed Test shall be applied to the smallest gas-forming portion or portions of

—— any sample of drinking water upon which sufficient data are not available to justify the application of the Confirmed Test.

—— any sample of drinking water upon which the previous records indicate the inapplicability of the Confirmed Test.

—— any sample of drinking water which is being examined with reference to the U. S. Treasury Standard.

The Confirmed Test may be applied to the smallest gas-forming portion or to all portions showing gas, from

—— any sample of raw water, water in process of purification, or water prepared for human consumption where a sufficient number of prior examinations have established a satisfactory correlation of the Confirmed Test with the Completed Test.

—— miscellaneous samples from any other source where it is known that the Presumptive Test is too broadly inclusive.

The Presumptive Test may be applied to the smallest gas-forming portion or portions

—— in examination of sewage, sewage effluents, or water showing relatively high pollution, where fitness for use as drinking water is not under consideration, and

—— in the routine examination of raw waters in purification plants, provided that records indicate that the Presumptive Test is not too inclusive for the production of data statistically comparable to that obtained upon the finished water.

The above procedure is too troublesome for a laboratory handling large numbers of routine samples. The work is too great and the time too long for the value of the results. It was adopted because of the fact that *B. welchii*, a spore-forming group (though probably of fecal origin), also forms gas in

lactose media. *B. welchii* is obligate anaërobic, gram positive, esculin negative, and a spore-former. It may easily be differentiated from *B. coli* by its appearance in a hanging drop. (Prepare hanging drop by placing a drop of salt solution, 0.85% sodium chloride, on a sterile coverglass and mix with a minutè portion of the culture, taken direct from the fermentation tube. Invert this cover slip over a hollow slide, sealed by a ring of vaseline, and examine under the microscope.) It is a large, non-motile bacillus, occurring in chains particularly when grown in lactose bile media, as mentioned in the 1912 edition of "Standard Methods." In a few instances aërobic spore-forming bacilli have been described which fermented lactose broth, but such instances are extremely rare, and they have not been found in lactose bile.

In 1920 the lactose bile medium was improved by the additions of Brilliant-Green which dye eliminates spore-formers of the *B. welchii* type. Originally the proportion of dye was 1/10,000 in 5% bile media. Extensive work by Committees of the American Water Works Association and the American Public Health Association has resulted in the development of a somewhat more delicate medium by using 1/75,000 Brilliant-Green in 2% bile as the final dilutions after addition of the water to be tested. The Department of Water Supply Laboratories of New York City have since establishment in 1897 relied upon presumptive tests for the *B. coli* group without confirmation to safeguard the supply. The media used have been improved from time to time. Since 1920 Brilliant-Green bile has been used because of its elimination of *B. welchii*. Beginning July 1st, 1933, the new formula recently standardized, 2% bile and 1/75,000 Brilliant-Green, has been used. Requirement of 10% minimum amount of gas formed has been retained for two reasons: first, possible inversion of a small amount of lactose to dextrose during autoclave sterilization and, second, the fact that vigorous forms of *B. welchii* may produce as much as 10% gas in this medium containing such a reduced quantity of Brilliant-Green.

Brilliant-Green bile gives a true comparative picture of the quality of the water supply from the watershed to the distribution system. In freshly polluted waters it eliminates practically none of the coli-aerogenes group and may surpass lactose broth. In stored and chlorinated waters attenuated forms of *B. coli* are eliminated. The author lays great sanitary stress upon this fact. Numerous investigations including those at Mt. Prospect Laboratory and those of the late Alexander Houston of London have shown that in two weeks time 90–99% of *B. typhi* contamination of water is eliminated and in two months time practically all *B. typhi*. The rapidity of gas formation is largely governed by attenuation of the bacilli. Gas formation on the second day with none or only a small amount on the first day indicates generally contamination beyond two weeks previous and three days' requirement for 10% gas may mean as much as a two months interval. The presence of the coli-aerogenes group may mean presence of animal as well as human contamination. There is no method of distinguishing between the two sources. The presence of human contamination means only the possibility of typhoid bacteria since less than 1% of the population are typhoid carriers. There is therefore a very large factor of safety in judging the sanitation of a water from the presence or absence of the coli-aerogenes group and elimination of attenuated forms of *B. coli* is decidedly important. Numerous comparisons between presumptive and completed tests have been made so that possible error is known. An enormous amount of

work is eliminated by the above presumptive use of Brilliant-Green bile, in addition to saving of media, equipment, incubator space, and force. That the above procedure has been safe in the case of the City of New York is shown by the extremely low typhoid death rate of 0.3 (1937) per hundred thousand population, and the fact that since 1907 particularly since starting of chlorination no cases of typhoid fever have been traced to the water supply nor has it been under suspicion.

In testing for *B. coli* 0.1 ml., 1 ml., and 10 ml. portions of water are introduced to the bottom of the bile tubes, or in polluted waters quantities varying by decimal multiples or fractions until a negative test is obtained. At important chlorination stations 100 ml. portions of water are examined. Sewage will usually show a positive test in 0.000001 ml. The plantings are made at the same time that the plates are prepared for total counts. The tubes are incubated at 37° C. for three days. 10% of gas within three days is a positive test. Tubes showing no gas in two days are discarded.

Examination for B. Typhi, etc.

Hesse agar is retained in the text as a possible simple method of isolation of *B. typhi* from water supply because it was successfully used to accomplish this purpose several times following its development. This was true by use of even small amounts of water such as 1 ml. Preliminary use of bile media precedes the test on the agar.

The water laboratories of London, England, have successfully isolated *B. typhi* and *B. paratyphi-B* from sewage and water by methods described in the annual reports of former Director of Laboratories Alexander Houston. The reports should be consulted for details, particularly the 26th Annual Report, Metropolitan Water Board for 1931, pages 26, 27, and 31, for isolation of *B. paratyphoid-B*.

This test is only made in cases of special investigation.

Direct test for *B. typhi* may be made from the bile tubes or from larger quantities of water incubated in bottles of bile.[8] Dilutions from the inoculated bile media are mixed with 10 ml. melted Hesse agar (see Preparation of Media) in petri dishes with porous tops. The poured plates are hardened in the ice-box and then incubated 24 hours at 37° C. The colony is characteristic only when a few colonies are on a plate. They are large size, have a dense white nucleus, then translucent zone, then dense white seam. The colonies are perfectly round. They retain their appearance if placed in the ice-box, and as they develop further produce another translucent area and another seam, etc., giving the appearance of concentric rings. Other large colonies of other species usually become dense throughout. Forms most likely to interfere are *B. paratyphi, B. pyocyaneous, B. fluorescens liquefaciens,* and some very motile forms of *B. coli.*

From the edges of the colony direct tests should be made for *B. typhi* and *B. para-typhi* by specific agglutination tests.

Transplants may be made to Endo media instead of Hesse agar and the colorless colonies picked for the identifying tests.

[8] In the latter case it is preferable to omit lactose from the bile media.

Widal Test.—To make the Widal test place a small portion of the culture in a drop of normal salt solution on a cover glass, and invert it over a rubber ring on a glass slide, using vaseline on the edges so as to prevent evaporation and consequent movement by currents in the drop.

If the bacteria are motile rods resembling *B. typhi* add a drop of equal size of highly diluted anti-typhoid serum (the latter diluted with physiological salt solution). If in the course of half an hour the bacteria cease their motions and agglutinate, the presence of *B. typhi* is practically established. In rare cases, some strains of *B. coli* and allied species may respond to the Widal test, but almost invariably in dilutions of 1–50 or less. The high-power dry lens is best for this work.

To determine the point of highest dilution at which agglutination takes place the Widal test is best made in tubes and examined macroscopically. Place a series of small test tubes in a rack and pour into each varying dilutions of anti-typhoid serum. To each tube add an equal amount of 24-hour broth culture of *B. typhi* and incubate at 37° C. for at least three hours. The highest dilution at which precipitation takes place is the highest point of agglutination.

Russell Media.—As additional rapid means of differentiating between *B. typhi* and *B. para-typhi* A and B, needle stabs may be made into tubes of Russell media (see Preparation of Media) and incubated at 37° C. The reactions are based on the fact that the bacilli growing aërobically, that is on the slant, only utilize the carbohydrate when present in amounts over 0.1%, whereas, growing anaërobically stabbed in the butt, they must utilize the carbohydrates for their oxygen supply and therefore ferment the trace of glucose present. The indications of the Russell media reactions are as follows:

B. coli Group—Russell media—Slant, acid (Glucose, acid and gas)
Butt, acid and gas (Lactose, acid and gas)

B. typhi Group *B. dysentery* Group	Russell media	Slant unchanged	(Glucose, acid only)
		Butt, acid only	(Lactose, not fermented)
B. paratyphi Group *B. enteritidis* Group	Russell media	Slant unchanged	(Glucose, acid and gas)
		Butt, acid and gas	(Lactose, not fermented)

B. alkaligenes Group—Russell media—Slant unchanged (Glucose, not fermented)
Butt unchanged (Lactose, not fermented)

In distinguishing between typhoid and dysentery (true or Shiga type)—typhoid bacilli are motile, dysentery non-motile, typhoid produces acid in mannite, dysentery does not.

There also exist three types of para-dysentery (non-motile): Type I (Park-Hiss), type II (Flexner) and type III (Strong). Para-dysentery are different from true dysentery in that they produce acid with mannite (the same as typhoid) but they all give positive indol, while dysentery and typhoid do not. Indol is sometimes doubtful with Flexner. The three para-dysentery groups are further distinguished among themselves by their reactions upon maltose

and saccharose. The type I produces acid in neither, type II produces acid in maltose but not in saccharose, type III produces acid in saccharose but not in maltose. The usual final test for all these different types of typhoid and dysentery is the agglutination with specific serums. The sugar fermentation tests must be made upon freshly isolated cultures since after artificial cultivation Park-Hiss strains may ferment maltose and Flexner strains saccharose as demonstrated by Hiss and by Lentz.

The members of the typhoid, para-typhoid, dysentery and para-dysentery groups all form colorless colonies upon Endo media. This is frequently the starting point for isolation.

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MISCELLANEOUS ANALYSES*

ANALYSIS OF ACETONE[1]

PURITY

Reagents.—*N/20 $Na_2S_2O_3$* is made up and standardized carefully against $K_2Cr_2O_7$. For accurate work standardized burettes must be used and burette corrections and temperature corrections applied.

N/10 Iodine is made up and is standardized at the time of making a determination The standardization consists in titrating against the N/20 $Na_2S_2O_3$ 50 ml. of iodine mixed with the same amounts of NaOH and H_2SO_4 as are used in the determination of acetone. The titrations are made in triplicate and the average of the three with burette and temperature corrections is used as the blank in making the calculation.

Normal NaOH is made up and standardized against 2 N sulfuric acid.

2 N Sulfuric Acid is made up and checked against 1 N NaOH and the strength adjusted so that 25 ml. of the acid will neutralize 50 ml. of the NaOH.

Starch Solution is prepared according to standard procedure.

Preparation of Sample.—Approximately 1.4 grams of acetone are carefully weighed by one of the following methods and made up to a volume of one liter.

(*a*) Glass ampules $\frac{5}{8}''$ to $\frac{3}{4}''$ in diameter are blown and after filling with acetone are sealed. The exact weight of sample is determined by the difference in weight of the empty and filled ampule. Samples varying in weight more than plus or minus 0.1 gram from 1.4 gram should be rejected. The glass ampules are dropped into 500 ml. glass-stoppered bottles containing 200 ml. of boiled distilled water and broken by shaking. The capillary stem is then carefully crushed with a glass rod to allow thorough washing out of the acetone and the sample and combined washings made up to one liter at 20° C.

(*b*) A quicker, easier method is to weigh out 1.75 ml. of acetone from a 2 ml. pipette graduated in tenths of a ml. into a small glass-stoppered weighing bottle, conical shape, capacity 12 to 51 ml. (as listed in Eimer and Amend's catalogue. This volume will weigh approximately 1.4 grams. The weighing bottle is inverted and the mouth held under the surface of boiled distilled water in a liter beaker. The stopper is then removed under water by means of a glass rod with a hook on the end. The bottle is thoroughly washed out and the water and acetone are transferred to a one liter flask and made up to the mark at 20° C.

Procedure.—Three 25 ml. aliquots from each of 3 flasks made up according to (*a*) or (*b*) under Preparation of Sample are pipetted into 750-ml. Erlenmeyer flasks containing 50 ml. of the 1 N NaOH solution. A Bureau of Standards pipette is used for taking the samples from the flasks. Into each flask is run with constant shaking 50 ml. of the N/10 Iodine. The flasks are then stoppered and allowed to stand at about 20° C. (cooling necessary in warm weather) for at

* Edited by N. H. Furman.

[1] Method of Commercial Solvents Corporation.

least 20 minutes. At the end of this time 26 ml. of the 2 N sulfuric acid are poured into the first flask which is then titrated *immediately* against N/20 $Na_2S_2O_3$. The solution must be acid before any thiosulfate is added, otherwise the determination is ruined. When the color of the iodine has almost faded out, starch solution is added and the titration continued until the blue color disappears and the bright yellow color of the iodoform suspension is reached. The mls. of thiosulfate are read, the burette and temperature corrections are applied and the corrected reading subtracted from the average corrected blank. Percentage of dimethyl ketone by weight is then calculated from the following formula:

$$\frac{(\text{ml. } Na_2S_2O_3 \text{ for blank} - \text{ml. } Na_2S_2O_3 \text{ for sample}) \times N \times .9675 \times 40}{\text{Weight of acetone taken for dilution}} = \%\ CO(CH_3)_2 \text{ by weight.}$$

The following precautions must be observed:

1. Only boiled distilled water should be used in preparing the solutions and throughout the determination.

2. Standardized glassware must be used and burette and temperature corrections must be applied to all readings.

3. Weight of sample taken and amount of iodine solution used must be as specified. With these amounts the 35 to 40% excess of iodine, found to be optimum for completion of the iodoform reaction, will be present. Use of the small glass-stoppered bottle described in (*b*) under Preparation of the Sample with the 2 ml. pipette insures uniformity in the weight of sample taken.

4. The iodine solution must be added slowly and with constant shaking. The Bureau of Standards calibrated burettes with fine tip and delivery time of approximately 2 minutes have been found very satisfactory.

5. A slight excess of acid must be added just before the titration with thiosulfate. Too great an excess will give low results.

Specific Gravity.—The specific gravity is determined at 20/20° C. using a standardized pycnometer.

Acidity.—Add 50 ml. of the sample to 50 ml. of neutral distilled water in a 300 ml. Erlenmeyer flask and titrate with N/100 NaOH to a faint pink coloration using phenolphthalein as indicator.

$$\frac{\text{ml. NaOH} \times N \times 2.2}{39.7} = \%\ \text{acid as } CO_2,$$

where

N = Normality of NaOH,
39.7 = Weight of 50 ml. sample (Sp.gr. .795).

Water.—Shake together one volume of the sample and three volumes of benzene in a test tube. Any water present will be precipitated by the benzene thus imparting a turbidity to the solution in the tube.

Color.—The sample is compared with a sample of distilled water. It should be absolutely colorless with no cloudiness or solid matter.

Residue.—Evaporate 25 ml. of the sample to dryness in a tared porcelain or preferably a tared platinum crucible over a water bath. Dry to constant weight at 110° C. in an oven.

$$\frac{\text{Weight of residue}}{\text{Weight of sample}} \times 100 = \% \text{ Residue on Evaporation.}$$

Miscibility with Water.—A sample of acetone is shaken with various proportions of water. Report any turbidity and the ratio of acetone to water which gave it.

$KMnO_4$ Test.—1 ml. of 0.1% $KMnO_4$ solution is added to 100 ml. of the sample in a 200-ml. Florence flask and allowed to stand at 15.5° C. Report the time required for the permanganate color to fade. Allow to stand at least 5 hours, if fading does not come sooner.

Detection of Aldehydes in Acetone

Reagent.—Add a 10% solution of ammonia to a 5% solution of silver nitrate until the precipitate which is formed just redissolves. Keep in dark bottle.

Procedure.—Add 10 ml. of the sample to be tested to a test tube or small, tall form, weighing bottle and add to this 5 ml. of the above reagent. Shake and place immediately in a dark closet. It is necessary to shake the test tube vigorously every five minutes during the test. When viewed against a white background any precipitate or dark color after twenty minutes in the dark closet would indicate the presence of aldehydes.

ACETONE

ANALYSIS OF ACETONE BY MESSINGER'S METHOD

An amount of acetone in aqueous solution, equivalent to 30–40 mg., is pipetted or added to 50 ml. of N sodium hydroxide solution contained in a glass bottle which can be closed with a ground glass stopper. After standing for 5 minutes, about 25% excess of a 0.1 N solution of iodine is run in from a burette with continual shaking. It is essential to shake properly or to keep the liquid in continuous rotation. The excess of iodine is needed to complete the reaction.[2] The bottle is then stoppered and the solution allowed to stand for at least 10 minutes (20 minutes in cold weather).

Twenty-five ml. of 2 N sulfuric acid is then added from a measuring cylinder, 0.3–0.4 ml. being added in excess of the amount found necessary to neutralize the 50 ml. of caustic soda solution. A 0.05 N solution of sodium thiosulfate is then added from a burette until the yellow color just remains visible. Freshly prepared starch solution is now added and the titration finished. 1 ml. of 0.1 N iodine = 0.96747 mg. of acetone.

If a larger excess of sulfuric acid is added, too much thiosulfate is required, and the real amount of iodine solution required is thus reduced (see below).

[2] L. F. Goodwin, J. Am. Chem. Soc., **42**, 39 (1920).

If the bottle is not shaken vigorously while adding the iodine solution, the iodine cannot act completely on the acetone.

ALCOHOL

DETECTION AND ESTIMATION OF ALCOHOL

Detection of Alcohol.—Ethyl or " grain alcohol " C_2H_5OH boils at 78.4° C. so that it readily distills with steam. If an appreciable amount of alcohol is present in the liquor it may be detected by the odor of the solution or in the first fraction of its distillate.

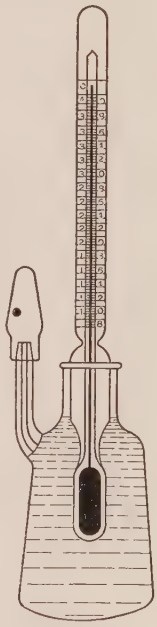

Fig. 297. Pycnometer.

Iodoform Test.—A few ml. of the liquor are distilled and to this distillate is added a small crystal of iodine or a few ml. of aqueous solution of iodine-potassium iodide solution, followed by sufficient potassium hydroxide to give the liquid a distinct yellow to brownish color. The solution is warmed gently. If alcohol is present a whitish to lemon yellow precipitate of iodoform will appear. The odor of iodoform may be noted. If the crystals form slowly they are deposited in form of perfect stars and hexagonal plates. This test is not conclusive of alcohol as other organic materials also give iodoform.

Berthelot's Test.—The distillate of the liquid is vigorously agitated with a few drops of benzoyl chloride and 4 or 5 drops of 10% solution of sodium hydroxide, until the penetrating odor of benzoyl chloride has disappeared. The characteristic odor of ethyl benzoate will be detected if alcohol is present in the liquid tested.

Reaction: $C_2H_5OH + C_6H_5 \cdot COCl + KOH = C_6H_5 \cdot CO \cdot OC_2H_5 + KCl + H_2O$.

Ethyl Acetate Test.—The liquid (distillate) is mixed with the same volume of concentrated sulfuric acid. A very small quantity of anhydrous (fused) sodium acetate is added and the mixture warmed. The odor of ethyl acetate will be recognized if alcohol was present in the liquid tested.

Reactions: $C_2H_5OH + H_2SO_4 = C_2H_5O \cdot SO_2 \cdot OH + H_2O$.

$C_2H_5O.SO_2.OH + CH_3.CO.ONa = CH_3.CO.OC_2H_5 + NaHSO_4$.

DETERMINATION OF ALCOHOL

In carbonated liquids the carbon dioxide should first be expelled by pouring the liquor back and forth from one beaker to another, or by vigorously shaking

the sample in a large separatory funnel and drawing off the lower portion, repeating this several times if necessary. After treatment the liquid should be free from foam.

Distillation Method.—This is the most accurate method for determination of alcohol. A convenient quantity of the sample is accurately measured or weighed, according to whether the per cent by weight or measure is desired. The weight taken varies from 25 to 100 grams, according to the alcohol content of the sample.

The sample is placed in a 250 to 400 ml. round-bottom flask and diluted to 150 ml. The flask is connected to a condenser and 90 to 95 ml. of the liquid is distilled into a narrow-necked flask. The distillate is made to exactly 100 ml. with distilled water.

The specific gravity of the thoroughly mixed distillate is taken by means of the pycnometer or by the Westphal balance, the temperature of the liquid being exactly 15.6° C. From the specific gravity the corresponding percentage of alcohol by weight or by volume, or the grams per 100 ml. in the distillate, is ascertained from the accompanying tables.

The percentage of alcohol by weight in the sample is obtained by multiplying the per cent by weight in the distillate by the weight of the distillate, and dividing by the weight of the sample taken. The per cent by volume is obtained by multiplying the per cent by volume in the distillate by 100 and dividing by the volume of the sample taken.

Evaporation Method.—Should a distillation apparatus not be available the following method may be used. The specific gravity of the original sample is determined, the temperature being regulated to 15.6° C. A measured portion of the liquor (50–100 ml.) is placed in a porcelain dish over a water bath and three fourths of its volume evaporated off. The concentrate is diluted to exactly its original volume and its specific gravity again taken at 15.6° C. To apply the table add 1 to the original specific gravity and from this total subtract the second specific gravity. The difference is the specific gravity corresponding to the alcohol in the liquor. For example, if the specific gravity of the original solution was 0.9989 and the de-alcoholized sample was 1.0005, then $1.9989 - 1.0005 = .9984 = 1.06\%$ alcohol, by volume.

If the liquor is free from residue its specific gravity may be taken directly without distillation and the alcohol content determined, provided it is a mixture of water and alcohol.

ANALYSIS OF GRAIN ALCOHOL (ETHYL ALCOHOL, SPIRITS OF WINE, COLOGNE SPIRITS)

Per cent Ethyl Alcohol.—The method of determining per cent of alcohol by the distillation of the alcohol from liquors has already been discussed. In straight grain alcohol the specific gravity may be taken directly by means of the Westphal balance or by means of the pycnometer and the amount of alcohol by weight or volume obtained from the tables on pages 2142–6.

Proof.—This is obtained by multiplying the per cent by volume of the ethyl alcohol by 2.

Non-volatile Residue.—100 ml. of the sample, in a large platinum (tared) dish, are evaporated on the water bath to a moist residue. The evaporation to

dryness is accomplished in a water oven for two and a half hours at 100° C. The weight of the residue divided by the specific gravity gives per cent of non-volatile residue.

Acidity Expressed as Acetic Acid.—10 ml. of the alcohol are titrated with N/10 NaOH in presence of phenolphthalein indicator.

1 ml. N/10 NaOH = 0.006 gram acetic acid.

Distilled Solution for Determining Aldehydes, Furfural and Esters (A). To 250 ml. of the sample 30 ml. of water are added and the liquor distilled into a 250-ml. volumetric flask. When the distillate has almost reached the mark the distillation is discontinued and the volume made up to mark by addition of water. The distillate contains all the aldehyde, furfural and esters. 1 ml. of this solution is equivalent to 1 ml. of the original sample.

ALDEHYDES

Qualitative Examination

Alkaline Silver Nitrate Reagent.—Three grams of $AgNO_3$ are dissolved in a little water in a 100-ml. volumetric flask, 3 grams of pure NaOH are added followed by 20 ml. of strong NH_4OH and the whole made to 100 ml.

Test.—Ten ml. of the sample are diluted with an equal volume of water in a glass stoppered bottle, 1 ml. of the alkaline silver reagent added, and the bottle is closed and placed in a dark chamber for an hour. The liquid is now filtered and the filtrate made acid with HNO_3 and a few drops of HCl added. A precipitate of AgCl indicates the non-reduction of the silver salt and consequently a negligible amount of aldehyde in the sample.

Quantitative Determination of Aldehyde

Reagents: ***Alcohol—Aldehyde-free.***—To 1.5 liters of 95% ethyl alcohol are added 25 grams of NaOH in a large distilling flask and all but 100 ml. distilled over. To this distillate are added 2.5 grams of meta-phenylenediamine hydrochloride, the sample being placed in a large flask with reflux condenser. After heating on a steam bath for several hours the solution is distilled down to about 200 ml. The distillate (rejecting the first 100 ml.) is placed in a stoppered bottle for use.

Fuchsin-Sulfite Solution.—To 0.5 gram of fuchsin dissolved in 500 ml. of water are added 5 grams of SO_2 dissolved in water. (100 ml. H_2O saturated with SO_2 at 20° C. contains 11.29 g. SO_2, at 15° C. = 13.5 g. SO_2—Seidell. Determine by titrating with N/10 iodine sol. 1 ml. = .0032 g. SO_2.) Dilute to 1000 ml. and allow to stand until colorless. The solution retains its strength only a few days, so should be made up in small quantities at a time.

Standard Acetaldehyde Solution.—Five grams of aldehyde ammonia are purified by repeated extraction with ether, grinding the salt with the ether in a mortar and decanting off the ether. The salt is dried by blowing air over it and finally placing it in a vacuum desiccator over concentrated H_2SO_4. 1.386 gram of the purified salt is dissolved in 50 ml. of the 95% alcohol reagent prepared as stated above. To this are added 22.7 ml. of N alcoholic H_2SO_4

(49.04 grams H_2SO_4 made up to 1000 ml. with 95% alcohol) and the solution made to 100 ml. with 95% alcohol. To compensate for the $(NH_4)_2 SO_4$ precipitated 0.8 ml. alcohol is added. After standing all night the solution is filtered. 100 ml. of this reagent contains 1 gram of acetaldehyde. It retains its strength

Reagent for Standard.—Two ml. of the above solution diluted with 50% alcohol to 100 ml. 1 ml. contains 0.0002 gram acetaldehyde. Make up fresh for use.

Procedure for Aldehydes

Ten ml. of the solution *A* are diluted to 50 ml. with the aldehyde free alcohol (diluted to 50% by volume), 25 ml. of fuchsin reagent are added and the mixture allowed to stand for 15 minutes (all reagents and the sample should be at 15° C.). The solution is now compared colorimetrically with standards made up in the same way. Nessler tubes may be used. Comparison may be made in a colorimeter. From this the per cent aldehyde is readily calculated.

Determination of Furfural

Standard Furfural Reagents.—One gram of freshly redistilled furfural is dissolved in 100 ml. 95% alcohol (furfural free). This solution keeps.

One ml. of the strong solution is diluted to 100 ml. with 50% (by volume) alcohol. 1 ml. = 0.0001 gram furfural.

Procedure.—Twenty ml. of the distilled solution (*A*) are diluted to 50 ml. with 50% (by volume) of furfural-free alcohol. To this are added 2 ml. of colorless aniline and 0.5 ml. of dilute HCl (5 : 4) and the mixture placed in a water bath at 15° C. for fifteen minutes. Colorimetric comparison is now made with standards containing known amounts of furfural, the solutions being prepared in the same way as the sample.

Determination of Esters Expressed as Ethyl Acetate

Fifty ml. of the distilled solution (*A*) in an Erlenmeyer flask are exactly neutralized with N/10 NaOH (phenolphthalein indicator) and about 50 ml. excess added, the exact amount being recorded. The solution is boiled for an hour with reflux condenser. After cooling, the excess of alkali is titrated with N/10 acid. The ml. N/10 NaOH consumed in the saponification, multiplied by 0.0088, gives the gram weight of esters calculated as ethyl acetate. This weight divided by the specific gravity of the sample and multiplied by 2 gives per cent.

Determination of Fusel Oil

Fifty ml. of the original sample, in an Erlenmeyer flask, are diluted with an equal volume of water and 20 ml. of N/5 NaOH added. The mixture is now saponified by boiling for an hour with reflux condenser. The flask is connected to a condenser and about 90 ml. distilled into a deep beaker. 25 ml. of water are added to the flask and the distillation continued until the total volume of the distillate is 115 ml. Finely ground salt (NaCl) is now added until the solution is almost saturated and a saturated solution of NaCl added until the

specific gravity of the solution is 1.10. The solution placed in a separatory funnel is extracted four times with carbon tetrachloride, CCl_4, using 40, 30, 20 and 10 ml. CCl_4 respectively. To the extract in a separatory funnel 10 ml. of KOH solution (1 : 1) are added. This solution is cooled in ice water to 0° C. and at the same time 100 ml., accurately measured, of $KMnO_4$ solution (20 grams per liter) in a flask. When cooled to 0° C. the bulk of the $KMnO_4$ solution is added to the extract, leaving the rinsing out of the flask until later. The mixture removed from the ice bath is shaken vigorously for five minutes, then set aside for half an hour allowing it to warm up to room temperature (20–25° C.).

Into a liter Erlenmeyer flask are measured accurately 100 ml. of H_2O_2 solution (2% stronger than the $KMnO_4$ solution) followed by 100 ml. of 25% H_2SO_4 and to this mixture are added slowly the contents of the separatory funnel, swirling to get an even distribution. (The acid solution should be constantly in excess.) The rinsing of the separatory funnel and the flask containing the residue of the $KMnO_4$ are added and the excess of the H_2O_2 determined by titration with standard $KMnO_4$ solution (10 grams $KMnO_4$ per liter).

Blank.—The same amounts of stronger $KMnO_4$, KOH, H_2O_2 and H_2SO_4 are mixed side by side with the sample and the residual H_2O_2 determined with the standard $KMnO_4$ to determine the blank. This is subtracted from the first titration and the difference multiplied by the value of the standard $KMnO_4$. If this is exactly 10 grams per liter as determined by titration with N $H_2C_2O_4$ then—

1 ml. $KMnO_4$ = 0.696 gram amyl alcohol. ($KMnO_4$ 10 g. per liter.)

Note.—1 ml. N $H_2C_2O_4$ = 0.03161 g. $KMnO_4$. The standard $KMnO_4$ should contain 0.01 g. per ml. of the reagent.

Detection of Nitrates in Grain Alcohol

Fifty ml. of the sample are neutralized with N/10 NaOH (phenolphthalein indicator) and evaporated to a moist residue. A little distilled water is added 1 ml. of phenoldisulfonic acid, and the mix made alkaline with NH_4OH. A bright orange color indicates the presence of nitrates. Run a blank on the water used. See subject of nitrates in the chapter on Water Analysis.

Determination of Sulfur Compounds in Grain Alcohol

A hundred ml. of the alcohol are made slightly alkaline with N/10 NaOH (phenolphthalein) and 5 ml. H_2O_2 added, preferably in a large platinum dish. The residue is ignited over an alcohol flame, then taken up with 50 ml. of water, 5 ml. dilute HCl added and 5 ml. 10% $BaCl_2$. The precipitated $BaSO_4$ is filtered off, ignited and weighed according to the customary procedure.

$$BaSO_4 \times 0.1373 = S.$$

Determination of Methyl Alcohol, Wood Spirit, Wood Naphtha, Wood Alcohol, Etc.

See Methyl Alcohol in section following the tables on alcohol.

PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT*

GILPIN, DRINKWATER, AND SQUIBB

Specific Gravity at 60° / 60° F.	Alcohol			Specific Gravity at 60° / 60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 ml.		per cent by volume.	per cent by weight.	Grams per 100 ml.
1.00000	0.00	0.00	0.00	.99473	3.60	2 88	2.86
0.99984	0.10	0.08	0.08	.99459	3.70	2.96	2.94
.99968	0.20	0.16	0.16	.99445	3.80	3.04	3.02
.99953	0.30	0.24	0.24	.99431	3.90	3.12	3.10
.99937	0.40	0.32	0.32	.99417	4.00	3.20	3.18
.99923	0.50	0.40	0.40	.99403	4.10	3.28	3.26
.99907	0.60	0.48	0.48	.99390	4.20	3.36	3.34
.99892	0.70	0.56	0.56	.99376	4.30	3.44	3.42
.99877	0.80	0.64	0.64	.99363	4.40	3.52	3.50
.99861	0.90	0.71	0.71	.99349	4.50	3.60	3 58
.99849	1.00	0.79	0.79	.99335	4.60	3.68	3.66
.99834	1.10	0.87	0.87	.99322	4.70	3.76	3.74
.99819	1.20	0.95	0.95	.99308	4.80	3.84	3.81
.99805	1.30	1.03	1.03	.99295	4.90	3.92	3.89
.99790	1.40	1.11	1.11	.99281	5.00	4.00	3.97
.99775	1.50	1.19	1.19	.99268	5.10	4.08	4.05
.99760	1.60	1.27	1.27	.99255	5.20	4.16	4.13
.99745	1.70	1.35	1.35	.99241	5.30	4 24	4.21
.99731	1.80	1.43	1.43	.99228	5.40	4.32	4.29
.99716	1.90	1.51	1.51	.99215	5.50	4.40	4.37
.99701	2.00	1.59	1.59	.99202	5.60	4.48	4.44
.99687	2.10	1.67	1.66	.99189	5.70	4.56	4.52
.99672	2.20	1.75	1.74	.99175	5.80	4.64	4.60
.99658	2.30	1.83	1.82	.99162	5.90	4.72	4.68
.99643	2.40	1.91	1.90	.99149	6.00	4.80	4.76
.99629	2.50	1.99	1.98	.99136	6.10	4.88	4.84
.99615	2.60	2.07	2.06	.99123	6.20	4.96	4.92
.99600	2.70	2.15	2.14	.99111	6.30	5.05	5.00
.99586	2.80	2.23	2.22	.99098	6.40	5.13	5.08
.99571	2.90	2.31	2.30	.99085	6.50	5.21	5.16
.99557	3.00	2.39	2.38	.99072	6.60	5.29	5.24
.99543	3.10	2.47	2.46	.99059	6.70	5.37	5.32
.99529	3.20	2.55	2.54	.99047	6.80	5.45	5.40
.99515	3.30	2.64	2.62	.99034	6.90	5.53	5.48
.99501	3.40	2.72	2.70	.99021	7.00	5.61	5.56
.99487	3.50	2.80	2.78	.99009	7.10	5.69	5.64
.98996	7.20	5.77	5.72	.98513	11.30	9.11	8.97
.98984	7.30	5.86	5.80	.98502	11.40	9.19	9.05
.98971	7.40	5.94	5.88	.98491	11.50	9.27	9.13
.98959	7.50	6.02	5.96	.98479	11.60	9.35	9.21
.98947	7.60	6.10	6.04	.98468	11.70	9.43	9.29
.98934	7.70	6.18	6.11	.98457	11.80	9.51	9.36
.98922	7.80	6.26	6.19	.98446	11.90	9.59	9.44
.98909	7.90	6.34	6.27	.98435	12.00	9.67	9.52
.98897	8.00	6.42	6.35	.98424	12.10	9.75	9.60
.98885	8.10	6.50	6.43	.98413	12.20	9.83	9.68
.98873	8.20	6.58	6.51	.98402	12.30	9.92	9.76
.98861	8.30	6.67	6.59	.98391	12.40	10 00	9.84
.98849	8.40	6.75	6.67	.98381	12.50	10.08	9.92
.98837	8.50	6.83	6.75	.98370	12.60	10.16	10.00

* Bulletin No. 65, U. S. Department of Agriculture.

PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT

(Continued)

Specific Gravity at 60° / 60° F.	Alcohol			Specific Gravity at 60° / 60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 ml.		per cent by volume.	per cent by weight.	Grams per 100 ml.
.98825	8.60	6.91	6.83	.98359	12.70	10.24	10.07
.98813	8.70	6.99	6.91	.98348	12.80	10.33	10.15
.98801	8.80	7.07	6.99	.98337	12.90	10.41	10.23
.98789	8.90	7.15	7.07	.98326	13.00	10.49	10.31
.98777	9.00	7.23	7.14	.98315	13.10	10.57	10.39
.98765	9.10	7.31	7.22	.98305	13.20	10.65	10.47
.98754	9.20	7.39	7.30	.98294	13.30	10.74	10.55
.98742	9.30	7.48	7.38	.98283	13.40	10.82	10.63
.98730	9.40	7.56	7.46	.98273	13.50	10.90	10.71
.98719	9.50	7.64	7.54	.98262	13.60	10.98	10.79
.98707	9.60	7.72	7.62	.98251	13.70	11.06	10.87
.98695	9.70	7.80	7.70	.98240	13.80	11.15	10.95
.98683	9.80	7.88	7.78	.98230	13.90	11.23	11.03
.98672	9.90	7.96	7.85	.98219	14.00	11.31	11.11
.98660	10.00	8.04	7.93	.98209	14.10	11.39	11.19
.98649	10.10	8.12	8.01	.98198	14.20	11.47	11.27
.98637	10.20	8.20	8.09	.98188	14.30	11.56	11.35
.98626	10.30	8.29	8.17	.98177	14.40	11.64	11.43
.98614	10.40	8.37	8.25	.98167	14.50	11.72	11.51
.98603	10.50	8.45	8.33	.98156	14.60	11.80	11.59
.98592	10.60	8.53	8.41	.98146	14.70	11.88	11.67
.98580	10.70	8.61	8.49	.98135	14.80	11.97	11.75
.98569	10.80	8.70	8.57	.98125	14.90	12.05	11.82
.98557	10.90	8.78	8.65	.98114	15.00	12.13	11.90
.98546	11.00	8.86	8.73	.98104	15.10	12.21	11.98
.98535	11.10	8.94	8.81	.98093	15.20	12.29	12.06
.98524	11.20	9.02	8.89	.98083	15.30	12.38	12.14
.93073	15.40	12.46	12.22	.97658	19.50	15.84	15.47
.93063	15.50	12.54	12.30	.97648	19.60	15.93	15.55
.93052	15.60	12.62	12.37	.97638	19.70	16.01	15.63
.93042	15.70	12.70	12.45	.97628	19.80	16.09	15.71
.93032	15.80	12.79	12.53	.97618	19.90	16.18	15.79
.93021	15.90	12.87	12.61	.97608	20.00	16.26	15.87
.93011	16.00	12.95	12.69	.97598	20.10	16.34	15.95
.93001	16.10	13.03	12.77	.97588	20.20	16.42	16.03
.97991	16.20	13.12	12.85	.97578	20.30	16.51	16.10
.97980	16.30	13.20	12.93	.97568	20.40	16.59	16.18
.97970	16.40	13.29	13.01	.97558	20.50	16.67	16.26
.97960	16.50	13.37	13.09	.97547	20.60	16.75	16.34
.97950	16.60	13.45	13.17	.97537	20.70	16.84	16.42
.97940	16.70	13.53	13.25	.97527	20.80	16.92	16.50
.97929	16.80	13.62	13.33	.97517	20.90	17.01	16.58
.97919	16.90	13.70	13.41	.97507	21.00	17.09	16.66
.97909	17.00	13.78	13.49	.97497	21.10	17.17	16.74
.97899	17.10	13.86	13.57	.97487	21.20	17.26	16.82
97889	17.20	13.94	13.65	.97477	21.30	17.34	16.90
.97879	17.30	14.03	13.73	.97467	21.40	17.43	16.98
.97869	17.40	14.11	13.81	.97457	21.50	17.51	17.06
.97859	17.50	14.19	13.89	.97446	21.60	17.59	17.14
.97848	17.60	14.27	13.96	.97436	21.70	17.67	17.22
.97838	17.70	14.35	14.04	.97426	21.80	17.76	17.30
.97828	17.80	14.44	14.12	.97416	21.90	17.84	17.38
.97818	17.90	14.52	14.20	.97406	22.00	17.92	17.46

PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT

(Continued)

Specific Gravity at 60° / 60° F.	Alcohol			Specific Gravity at 60° / 60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 ml.		per cent by volume.	per cent by weight.	Grams per 100 ml.
.97808	18.00	14.60	14.28	.97396	22.10	18.00	17.54
.97798	18.10	14.68	14.36	.97386	22.20	18.09	17.62
.97788	18.20	14.77	14.44	.97375	22.30	18.17	17.70
.97778	18.30	14.85	14.52	.97365	22.40	18.26	17.78
.97768	18.40	14.94	14.60	.97355	22.50	18.34	17.86
.97758	18.50	15.02	14.68	.97345	22.60	18.42	17.94
.97748	18.60	15.10	14.76	.97335	22.70	18.51	18.02
.97738	18.70	15.18	14.84	.97324	22.80	18.59	18.10
.97728	18.80	15.27	14.92	.97314	22.90	18.68	18.18
.97718	18.90	15.38	15.00	.97304	23.00	18.76	18.26
.97708	19.00	15.43	15.08	.97294	23.10	18.84	18.33
.97698	19.10	15.51	15.15	.97283	23.20	18.92	18.41
.97688	19.20	15.59	15.23	.97273	23.30	19.01	18.49
.97678	19.30	15.68	15.31	.97263	23.40	19.09	18.57
.97668	19.40	15.76	15.39	.97253	23.50	19.17	18.65
.97242	23.60	19.25	18.73	.96805	27.70	22.71	21.98
.97232	23.70	19.34	18.81	.96794	27.80	22.79	22.06
.97222	23.80	19.42	18.88	.96783	27.90	22.88	22.14
.97211	23.90	19.51	18.96	.96772	28.00	22.96	22.22
.97201	24.00	19.59	19.04	.96761	28.10	23.04	22.30
.97191	24.10	19.67	19.12	.96749	28.20	23.13	22.38
.97180	24.20	19.76	19.20	.96738	28.30	23.21	22.45
.97170	24.30	19.84	19.28	.96726	28.40	23.30	22.53
.97159	24.40	19.93	19.36	.96715	28.50	23.38	22.61
.97149	24.50	20.01	19.44	.96704	28.60	23.47	22.69
.97139	24.60	20.09	19.52	.96692	28.70	23.55	22.77
.97128	24.70	20.18	19.60	.96681	28.80	23.64	22.85
.97118	24.80	20.26	19.68	.96669	28.90	23.72	22.93
.97107	24.90	20.35	19.76	.96658	29.00	23.81	23.01
.97097	25.00	20.43	19.84	.96646	29.10	23.89	23.09
.97086	25.10	20.51	19.92	.96635	29.20	23.98	23.17
.97076	25.20	20.60	20.00	.96623	29.30	24.06	23.25
.97065	25.30	20.68	20.08	.96611	29.40	24.15	23.33
.97055	25.40	20.77	20.16	.96600	29.50	24.23	23.41
.97044	25.50	20.85	20.24	.96587	29.60	24.32	23.49
.97033	25.60	20.93	20.32	.96576	29.70	24.40	23.57
.97023	25.70	21.02	20.40	.96564	29.80	24.49	23.65
.97012	25.80	21.10	20.47	.96553	29.90	24.57	23.73
.97001	25.90	21.19	20.55	.96541	30.00	24.66	23.81
.96991	26.00	21.27	20.63	.96529	30.10	24.74	23.89
.96980	26.10	21.35	20.71	.96517	30.20	24.83	23.97
.96969	26.20	21.44	20.79	.96505	30.30	24.91	24.04
.96959	26.30	21.52	20.87	.96493	30.40	25.00	24.12
.96949	26.40	21.61	20.95	.96481	30.50	25.08	24.20
.96937	26.50	21.69	21.03	.96469	30.60	25.17	24.28
.96926	26.60	21.77	21.11	.96457	30.70	25.25	24.36
.96915	26.70	21.86	21.19	.96445	30.80	25.34	24.44
.96905	26.80	21.94	21.27	.96433	30.90	25.42	24.52
.96894	26.90	22.03	21.35	.96421	31.00	25.51	24.60
.96883	27.00	22.11	21.43	.96409	31.10	25.60	24.68
.96872	27.10	22.20	21.51	.96396	31.20	25.68	24.76
.96861	27.20	22.28	21.59	.96384	31.30	25.77	24.84
.96850	27.30	22.37	21.67	.96372	31.40	25.85	24.92

PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT

(Continued)

Specific Gravity at 60°/60° F.	Alcohol			Specific Gravity at 60°/60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 ml.		per cent by volume.	per cent by weight.	Grams per 100 ml.
.96839	27.40	22.45	21.75	.96360	31.50	25.94	25.00
.96828	27.50	22.54	21.83	.96347	31.60	26.03	25.08
.96816	27.60	22.62	21.90	.96335	31.70	26.11	25.16
.96323	31.80	26.20	25.24	.95787	35.90	29.74	28.49
.96310	31.90	26.28	25.32	.95773	36.00	29.83	28.57
.96298	32.00	26.37	25.40	.95759	36.10	29.92	28.65
.96285	32.10	26.46	25.48	.95745	36.20	30.00	28.73
.96273	32.20	26.54	25.56	.95731	36.30	30.09	28.81
.96260	32.30	26.63	25.64	.95717	36.40	30.17	28.88
.96248	32.40	26.71	25.71	.95703	36.50	30.26	28.96
.96235	32.50	26.80	25.79	.95688	36.60	30.35	29.04
.96222	32.60	26.89	25.87	.95674	36.70	30.44	29.12
.96210	32.70	26.97	25.95	.95660	36.80	30.52	29.20
.96197	32.80	27.06	26.03	.95646	36.90	30.61	29.29
.96185	32.90	27.14	26.11	.95632	37.00	30.70	29.36
.96172	33.00	27.23	26.19	.95618	37.10	30.79	29.44
.96159	33.10	27.32	26.27	.95603	37.20	30.88	29.52
.96146	33.20	27.40	26.35	.95589	37.30	30.96	29.60
96133	33 30	27.49	26.43	.95574	37.40	31.05	29.68
.96120	33.40	27.57	26.51	.95560	37.50	31.14	29.76
.96108	33.50	27.66	26.59	.95545	37.60	31.23	29.84
.96095	33.60	27.75	26.67	.95531	37.70	31.32	29.92
.96082	33.70	27.83	26.75	.95516	37.80	31.40	30.00
.96069	33.80	27.92	26.82	.95502	37.90	31.49	30.08
.96056	33.90	28.00	26.90	.95487	38.00	31.58	30.16
.96043	34.00	28.09	26.98	.95472	38.10	31.67	30.24
.96030	34.10	28.18	27.06	.95457	38.20	31.76	30.32
.96016	34.20	28.26	27.14	.95442	38.30	31.85	30.40
.96003	34.30	28.35	27.22	.95427	38.40	31.94	30.48
.95990	34.40	28.43	27.30	.95413	38.50	32.03	30.56
.95977	34.50	28.52	27.38	.95398	38.60	32.12	30.64
.95963	34.60	28.61	27.46	.95383	38.70	32.20	30.72
.95950	34.70	28.70	27.54	.95368	38.80	32.29	30.79
.95937	34.80	28.78	27.62	.05353	38.90	32.37	30.87
.95923	34.90	28.87	27.70	.95338	39.00	32.46	30.95
.95910	35.00	28.96	27.78	.95323	39.10	32.55	31.03
.95896	35.10	29.05	27.86	.95307	39.20	32.64	31.11
.95883	35.20	29.13	27.94	.95292	39.30	32.72	31.18
.95869	35.30	29.22	28.02	.95277	39.40	32.81	31.26
.95855	35.40	29.30	28.09	.95262	39.50	32.90	31.34
.95842	35.50	29.38	28.17	.95246	39.60	32.99	31.42
.95828	35.60	29.48	28.25	.95231	39.70	33.08	31.50
.95814	35.70	29.57	28.33	.95216	39.80	33.17	31.58
.95800	35.80	29.65	28.41	.95200	39.90	33.27	31.66
.95185	40.00	33.35	31.74	.94519	44.10	37.02	34.99
.95169	40.10	33 44	31.82	.94502	44.20	37.11	35.07
.95154	40.20	33.53	31.90	.94484	44.30	37.21	35.15
.95138	40.30	33.61	31.98	.94467	44.40	37.30	35 23
.95122	40.40	33.70	32.06	.94450	44.50	37.39	35.31
.95107	40.50	33.79	32.14	.94433	44 60	37.48	35.39
.95091	40 60	33.88	32.22	.94416	44.70	35.57	35.47
.95075	40.70	33.97	32.30	.94398	44 80	37.66	35.55
.95059	40.80	34.06	32.38	.94381	44.90	37.76	35.63

PERCENTAGE OF ALCOHOL BY VOLUME AND BY WEIGHT*

(Continued)

Specific Gravity at 60°/60° F.	Alcohol			Specific Gravity at 60°/60° F.	Alcohol		
	per cent by volume.	per cent by weight.	Grams per 100 ml.		per cent by volume.	per cent by weight.	Grams per 100 ml.
.95044	40.90	34.15	32.46	.94364	45.00	37.84	35.71
.95028	41.00	34.24	32.54	.94346	45.10	37.93	35.79
.95012	41.10	34.33	32.62	.94329	45.20	38.02	35.87
.94996	41.20	34.42	32.70	.94311	45.30	38.12	35.95
.94980	41.30	34.50	32.78	.94294	45.40	38.21	36.03
.94964	41.40	34.59	32.86	.94276	45.50	38.30	36.11
.94948	41.50	34.68	32.93	.94258	45.60	38.39	36.19
.94932	41.60	34.77	33.01	.94241	45.70	38.48	36.26
.94916	41.70	34.86	33.09	.94223	45.80	38.57	36.34
.94900	41.80	34.95	33.17	.94206	45.90	38.66	36.42
.94884	41.90	35.04	33.25	.94188	46.00	38.75	36.50
.94868	42.00	35.13	33.33	.94170	46.10	38.84	36.58
.94852	42.10	35.22	33.41	.94152	46.20	38.93	36.66
.94835	42.20	35.31	33.49	.94134	46.30	39.03	36.74
.94810	42.30	35.40	33.57	.94116	46.40	39.12	36.82
.94802	42.40	35.49	33.65	.94098	46.50	39.21	36.90
.94786	42.50	35.58	33.73	.94080	46.60	39.30	36.98
.94770	42.60	35.67	33.81	.94062	46.70	39.39	37.06
.94753	42.70	35 76	33.89	.94044	46.80	39.49	37.13
.94737	42.80	35.85	33.97	.94026	46.90	39.58	37.21
.94720	42.90	35.94	34.04	.94008	47.00	39.67	37.29
.94704	43.00	36.03	34.12	.93990	47.10	39.76	37.37
.94687	43.10	36.12	34.20	.93971	47.20	39.85	37.45
.94670	43.20	36.21	34.28	.93953	47.30	39.95	37.53
.94654	43.30	36.30	34.36	.93934	47.40	40.04	37.61
.94637	43.40	36.39	34.44	.93916	47.50	40.13	37.69
.94620	43.50	36.48	34.52	.93898	47.60	40.22	37.77
.94603	43.60	36.57	34.60	.93879	47.70	40.32	37.85
.94586	43.70	36.66	34.68	.93861	47.80	40.41	37.93
.94570	43.80	36 75	34.76	.93842	47.90	40.51	38.01
.94553	43.90	36.84	34.84	.93824	48.00	40.60	38.09
.94536	44.00	36.93	34.91	.93805	48.10	40.69	38.17
.93786	48.20	40.78	38 25	.93617	49.10	41.61	38.96
.93768	48.30	40.88	38.33	.93598	49.20	41.71	39.04
.93749	48.40	40.97	38 41	.93578	49.30	41.80	39.12
.93730	48.50	41.06	38.49	.93559	49.40	41.90	39.20
.93711	48.60	41.15	38.57	.93540	49.50	41.99	39.28
.93692	48.70	41.24	38.65	.93521	49.60	42.08	39.36
.93679	48.80	41.34	38.72	.93502	49.70	42.18	39.44
.93655	48.90	41.43	38.80	.93482	49.80	42.27	39.52
.93636	49.00	41.52	38.88	.93463	49.90	42.37	39.60

* See additional tables in Chem. Annual, D. Van Nostrand Co.

THE ANALYSIS OF MIXTURES OF METHYL ACETATE, METHANOL AND WATER [3]

The percentage by weight of methyl acetate is determined in duplicate by saponification with alcoholic KOH solution using a Lunge weighing pipette for getting the exact weight of the sample.

The specific gravity of the liquid is then determined at 20/4° C. as found in the International Critical Tables; we have the following:

$$\frac{\text{100 grams of sample}}{\text{Sp.gr. at 20/4° C.}} = \text{Volume of 100 grams, } (A)$$

$$\frac{\%\ \text{MeAc by weight}}{0.933} = \text{Volume of MeAc in 100 grams. } (B)$$

Then

$$A - B = \text{Volume of MeOH} + H_2O \text{ in 100 grams, } (C)$$

$$\text{100 grams} - \%\text{MeAc by weight} = \text{Weight of MeOH} + H_2O \text{ in 100 grams } (D)$$

and

$$\frac{D}{C} = \text{Sp.gr. of MeOH} + H_2O \text{ mixture in the sample.}$$

Look up in specific gravity tables the percentages by weight of methanol and water corresponding to the specific gravity (D/C) as calculated.

NOTE.—This procedure was checked against known mixtures of pure methyl acetate, methanol and water and found to be fairly accurate within the range of 70 to 85% by weight of methyl acetate. It can be used for similar mixtures of the corresponding ethyl compounds.

METHYL ALCOHOL

DETECTION OF METHYL ALCOHOL—METHOD OF RICHE AND BARDY [4]

The following method for the detection of methyl alcohol in commercial spirit of wine depends on the formation of methylanilin violet:

Place 10 ml. of the sample, previously rectified over potassium carbonate if necessary, in a small flask with 15 grams of iodine and 2 grams of red phosphorus. Keep in ice water for from ten to fifteen minutes until action has

[3] Method of Commercial Solvents Corporation.
[4] Allen's Commercial Organic Analysis, 3d ed., 1: 80.

ceased. On a water bath distil the methyl and ethyl iodides formed into about 30 ml. of water. Wash with dilute alkali to eliminate free iodine. Separate the heavy oily liquid which settles and transfer to a flask containing 5 ml. of anilin. The flask should be placed in cold water, in case the action should be violent, or, if necessary, the reaction may be stimulated by gently warming the flask. After one hour boil the product with water and add about 20 ml. of a 15% solution of soda; when the bases rise to the top as an oily layer fill the flask up to the neck with water and draw them off with a pipette. Oxidize 1 ml. of the oily liquid by adding 10 grams of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate; mix thoroughly, introduce into a glass tube, and heat to 90° C. for eight or ten hours. Exhaust the product with warm alcohol, filter, and make up with alcohol to 100 ml. If the sample of spirits be pure the liquid is of a red tint, but in the presence of 1% of methyl alcohol it has a distinct violet shade; with 2.5% the shade is very distinct, and still more so with 5%. To detect more minute quantities of methyl alcohol, dilute 5 ml. of the colored liquid to 100 ml. with water, and dilute 5 ml. of this again to 400 ml. Heat the liquid thus obtained in porcelain and immerse a fragment of white merino wool (free from sulfur) in it for half an hour. If the alcohol be pure the wool will remain white, but if methylated the fiber will become violet, the depth of tint giving a fair approximate indication of the proportion of methyl alcohol present.

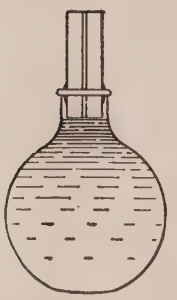

FIG. 298. Pycnometer.

DETECTION OF METHANOL (METHYL ALCOHOL) OXIDATION METHOD

Twenty-five ml. of the sample are diluted to about 100 ml. in a small distillation flask and about 10 grams of chromic acid added. Methyl alcohol, if present, is oxidized to formaldehyde. 15 to 20 ml. of the solution are distilled into a large test tube and a 5 to 10 ml. portion tested for formaldehyde by one of the methods outlined on the following page.

DETECTION OF METHANOL (WOOD ALCOHOL) IN THE PRESENCE OF ETHYL ALCOHOL [5]

Dilute 1 ml. of the alcohol with water to 100 ml. To 2 ml. of this solution add 2 ml. $KMnO_4$ (25 g. per l.) and 0.4 ml. 50% H_2SO_4. After 3 minutes destroy excess of $KMnO_4$ with oxalic acid, add 1 ml. of H_2SO_4 and 5 ml. of Schiff's fuchsin bisulfite reagent. In the presence of CH_3OH a violet color is produced on long standing (HCHO formed). Ethyl alcohol produces no color. 1% CH_3OH may be detected. 3% gives an intense color.

Reagent.—Schiff's Fuchsin Bisulfite—0.5 fuchsin in 500 ml. of water, add sufficient SO_2 to bleach the solution, make up to 1000 ml.

[5] A. Kling and A. Lassieur, C. A., 18, 1801 (1924).

FORMALDEHYDE

DETECTION OF FORMALDEHYDE [6]

Leach's Test.—The solution in which formaldehyde is suspected, obtained by distillation if necessary, is tested as follows: To a 10 ml. portion, in a casserole, an equal volume of pure milk is added followed by 10 ml. hydrochloric acid (sp.gr. 1.2) containing about 1 ml. of 10% ferric chloride solution per 500 of the acid. The mixture is heated to 80–90° C., the curd being broken up by agitation. A violet-colored solution indicates formaldehyde.

Hehner's Test.—Five ml. of the solution in a large test tube is mixed with about 50 ml. of pure milk, the tube tilted to a side and concentrated sulfuric acid carefully added so as to run down the wall of the tube without mixing with the milk. At the juncture of the acid and milk a violet color will appear if aldehyde is present.

Morphine-Sulfate Test.—To 5 ml. of morphine sulfate reagent [0.5 gram of morphine sulfate in 500 ml. sulfuric acid (sp.gr. 1.82)] a 2 ml. portion of the solution to be tested is added. The presence of formaldehyde is indicated by a violet color that develops on standing.

ESTIMATION OF FORMALDEHYDE IN SOLUTION

Formaldehyde, HCHO, is a gas sold in aqueous solution (37% HCHO or over). The solution generally contains alcohol to prevent polymerization.

DETERMINATION OF FORMALDEHYDE

Hydrogen Peroxide Method.[7]—To 50 ml. of normal NaOH in an Erlenmeyer flask are added 50 ml. of neutral H_2O_2 (3% sol.) and 3 ml. of the formaldehyde solution under examination, care being taken to add the sample with the tip of the measuring pipette near the surface of the reagents. A funnel is placed in the neck of the flask and the mixture heated for five minutes on the steam bath, with occasional shaking. The solution is now cooled, the funnel rinsed down, and the excess of N/NaOH titrated by normal H_2SO_4, in presence of purified litmus indicator

1 ml. N/NaOH = 0.03003 gram HCHO.

[6] Carry out the tests with blanks of pure ethyl alcohol and ethyl alcohol containing a little methyl alcohol.

[7] J. Assoc. Official Agr. Chemists, Methods of Analysis (1916), page 75.

GLYCEROL

There are two recognized methods for the determination of glycerol:

A. Acetin method, depending upon the conversion of glycerol to triacetin by means of acetic anhydride and sodium acetate and a quantitative saponification of the triacetin. This method is recommended by the International Committee on glycerol as giving results nearer the truth and should be employed for crude and refined glycerines of over 40% strength.

B. Bichromate method, which is based on the fact that glycerol is completely oxidized to CO_2 and H_2O by $K_2Cr_2O_7$ in presence of H_2SO_4. The method is applicable for determination of glycerines in soap lyes.

The following procedures are taken from the report as recommended.[8]

ACETIN PROCESS FOR THE DETERMINATION OF GLYCEROL[9]

Reagents Required

(**A**) **Best Acetic Anhydride.**—This should be carefully selected. A good sample must not require more than 0.1 ml. normal NaOH for saponification of the impurities when a blank is run on 7.5 ml. Only a slight color should develop during digestion of the blank.

The anhydride may be tested for strength by the following method: Into a weighed stoppered vessel, containing 10 to 20 ml. of water, run about 2 ml. of the anhydride, replace the stopper and weigh. Let stand with occasional shaking, for several hours, to permit the hydrolysis of all the anhydride; then dilute to about 200 ml., add phenolphthalein and titrate with N/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralization it is an indication that the anhydride is incompletely hydrolyzed and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 ml.) measure about 2 ml. of the sample, stopper, mix, cool and weigh. Wash the contents into about 200 ml. of cold water, and titrate the acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grams) and double the result, obtaining the ml. N/1 NaOH per 100 grams of the sample. 1 ml. N/NaOH equals 0.0510 anhydride.

(**B**) **Pure Fused Sodium Acetate.**—The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous.

[8] J. Ind. Chem. Eng., **3**, 679 (1911).
[9] J. Ind. Eng. Chem., **3**, 683 (1911).

(C) A Solution of Caustic Soda for Neutralizing, of about N/1 Strength, Free from Carbonate.—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(D) N/1 Caustic Soda Free from Carbonate.—Prepared as above and carefully standardized. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(E) N/1 Acid.—Carefully standardized.

(F) Phenolphthalein Solution.—0.5% phenolphthalein in alcohol and neutralized.

The Method

In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 ml., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of the glycerin. A Grethan or Lunge pipette will be found convenient. Add about 3 grams of the anhydrous sodium acetate, then 7.5 ml. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapor.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 ml. of distilled water free from carbon dioxide at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80° C., until the solution is complete, except for a few dark particles representing organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected.

Cool the flask and contents without loosening from the condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid-washed filter into a Jena glass flask of about 1 liter capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 ml. of phenolphthalein solution (*F*), then run in caustic soda solution (*C*) or (*D*) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the

alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 ml. or a calculated excess of N/1 NaOH (*D*) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with N/1 acid (*E*) until the pinkish yellow or chosen end-point color just remains.[10] A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end-point taken.

From the N/1 NaOH consumed calculate the percentage of glycerol (including acetylizable impurities) after making the correction for the blank test described below.

1 ml. N/1 NaOH = 0.03069 gram glycerol.

The coefficient of expansion for normal solutions is 0.00033 per ml. for each degree centigrade. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 ml. of the N/1 alkali (*D*), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent of the N/1 NaOH, however, the entire amount taken in the analysis, 50 ml., should be titrated after dilution with 300 ml. water free from carbon dioxide and without boiling.

Determination of the Glycerol Value of the Acetylizable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 ml. of water, washed into the acetylizing flask and evaporated to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol.

Instructions for Calculating the Actual Glycerol Content

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if any are present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present these are included in this figure.

Trimethylenglycol is more volatile than glycerine and can therefore be concentrated by fractional distillation. An approximation to the quantity can

[10] A precipitate at this point is an indication of the presence of iron or alumina, and high results will be obtained unless a correction is made as described below.

be obtained from the spread between the acetin and bichromate results on such distillates. The spread multiplied by 1.736 will give the glycol.

Bichromate Process for Glycerol Determination. Reagents Required

(**A**) **Pure potassium bichromate** powdered and dried in air free from dust or organic vapors, at 110° to 120° C. This is taken as the standard.

(**B**) **Dilute Bichromate Solution.**—7.4564 grams of the above bichromate are dissolved in distilled water and the solution made up to one liter at 15.5° C.

(**C**) **Ferrous Ammonium Sulfate.**—It is never safe to assume this salt to be constant in composition and it must be standardized against the bichromate as follows: dissolve 3.7282 grams of bichromate (*A*) in 50 ml. of water. Add 50 ml. of 50% sulfuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulfate, and titrate back with the dilute bichromate (*B*). Calculate the value of the ferrous salt in terms of bichromate.

(**D**) **Silver Carbonate.**—This is prepared as required for each test from 140 ml. of 0.5% silver sulfate solution by precipitation with about 4.9 ml. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used as an excess prevents rapid settling). Settle, decant and wash once by decantation.

(**E**) **Subacetate of Lead.**—Boil a 10% solution of pure lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(**F**) **Potassium Ferricyanide.**—A very dilute, freshly prepared solution containing about 0.1%.

The Method

Weigh 20 grams of the glycerine, dilute to 250 ml. and take 25 ml. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 ml. in most cases) of the basic lead acetate (*E*), allow to stand a few minutes, dilute with distilled water to 100 ml., and then add 0.15 ml. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 ml., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 ml. are ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 ml. of the dilute glycerine should be taken and purified with 6 ml. of the basic acetate). Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 ml. of the clear filtrate into a flask or beaker (previously cleaned with potassium bichromate and sulfuric acid). Add 12 drops of sulfuric acid (1 : 4) to precipitate the small excess of lead as sulfate. Add 3.7282 grams of the powdered potassium bichromate (*A*). Rinse down the bichromate with 25 ml. of water and let stand with occasional shaking until all the bichromate is dissolved (no reduction will take place in the cold).

Now add 50 ml. of 50% sulfuric acid (by volume) and immerse the vessel in

boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, until the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulfate (*C*), making spot tests on a porcelain plate with the potassium ferricyanide (*F*). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gram glycerol = 7.4564 grams bichromate.

1 gram bichromate = 0.13411 gram glycerol.

The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the residue at 160° C.

For complete analysis see Journal of Industrial and Engineering Chemistry, Sept., 1911, pages 679–683.

NOTES.—(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulfuric acid, as stipulated.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 ml.

(4) It is sometimes advisable to add a little potassium sulfate to insure a clear filtrate.

LIGHT OIL IN COKE-OVEN GAS [11]

USE OF ACTIVATED CARBON IN ITS DETERMINATION

The quantity of the light oil in coke-oven gas, before and after scrubbing with straw oil, is generally determined by passing a definite quantity of the gas through straw oil contained in a train of bottles packed in ice, and subsequently separating the light oil from the straw oil by distillation. The removal of the light oil from the gas approaches completeness only when the flow of gas is extremely slow, and under all conditions the method of procedure is cumbersome.

The light oil present in the gas may be determined readily and accurately by the absorption of the condensable vapor in a definite quantity of gas by activated carbon, with subsequent removal by distillation of the carbon with U. S. P. cresol. Carbon of activity 40 to 50, screened 8 to 14 mesh, is suitable.

Apparatus

The absorption requires a 0.1-cu. ft. gas meter and two activated carbon tubes complete. The carbon tubes are cylindrical containers, 1.5 in. in diameter and 12 in. in length over all, fitted with a 20-mesh screen in one end, with 1-in. breasts and screw caps on both ends. Four connecting caps consisting of 1-in. screw caps carrying $\frac{5}{16}$ x $\frac{3}{4}$-in. copper tubes soldered in the centers and

[11] By Arthur L. Davis, Standard Oil Company (Indiana), Wood River, Ill.

fitted with $\frac{1}{16}$-in. rubber gaskets are used on each carbon tube during the absorption proper.

The distillation of the enriched activated carbon with cresol to remove the light oil is made, using a 500-ml., round-bottom, side-neck, Pyrex distilling flask; a 4-in. ring burner; a 200° C. thermometer; a " Barrett standard " condenser; a 200-ml. separatory funnel graduated to 100 ml.; U. S. P. cresol; and sodium hydroxide solution of specific gravity 1.10 to 1.15.

Procedure

Absorption.—Place 300 ml. of activated carbon in each of the two carbon tubes. Screw a connecting cap with rubber gasket to each end of each tube, and tighten with a pair of combination pliers.

Connect the inlet of the wet gas meter to the gas sampling tube and allow gas to pass through for several minutes to insure a thorough displacement of air. Turn off the gas, set the indicating hands of the meter to the zero position. (*Caution:* See that the hands are reasonably loose before turning so that the driving shafts will not be twisted.) Connect the top of the first carbon tube to the outlet of the gas meter, the bottom of the first tube to the bottom of the second tube, and either allow the residual gas coming from the top of the second tube to escape or be conducted away by an attached exit tube. *Keep the tubes in a vertical position.*

Pass an amount of gas containing approximately 30 to 40 ml. of light oil through the absorption tubes, at the rate of 10 to 15 cu. ft. per hr. At the completion of the absorption note the volume of gas passed, the temperature of the gas, and the barometric pressure.

Distillation.—Place the enriched carbon from the first tube in a 500-ml., side-neck, Pyrex distilling flask, add 125 ml. of cresol, *mix thoroughly by shaking in the flask*, insert the thermometer in neck of the flask, and connect to a " Barrett standard " condenser. Heat carefully with the ring burner and distil at a moderate rate till the temperature of 180° C. is reached. Collect the distillate in the 200-ml. separatory funnel, which is graduated to 100 ml. Add 125 ml. of sodium hydroxide solution, specific gravity 1.10 to 1.15 (8 to 13%), and agitate thoroughly. Care should be taken to release the pressure of the gas which is often built up. Allow to stand for a few minutes, run off the sodium hydroxide solution, and record the volume of light oil obtained.

Repeat the foregoing procedure with the second carbon tube. Record the volume of light oil obtained separately.

The sum of the two volumes of light oil obtained above gives the total volume of light oil from the volume of gas passed at the temperature and barometric pressure recorded.

Calculation.—The amount of light oil present in the gas (volume corrected to 15.5° C. (760 mm.)) is calculated as follows:

Total volume of light oil $\times 0.264 =$ Gal. light oil per 1000 cu. ft. gas.

$$\text{Cu. ft. gas} \times \frac{288.5}{273 + \text{temp. °C.}} \times \frac{\text{Bar. press.}}{760}.$$

Reprinted from J. Ind. Eng. Chem., 15, 689 (1923).

Gal. light oil per 1000 cu. ft. × 12 = Gal. light oil per ton of coal. (One ton of coal produces approximately 12,000 cu. ft. of gas.)

Volume of Gas Required

In order that the time required for making an absorption may be fairly accurately determined before making a test, the volume of gas containing a certain amount of condensable vapor should be known. The volume of gas containing approximately 30 to 40 ml. of light oil is shown in the table.

In making routine analysis by this method it is advised that the determination of the gas entering the scrubbers and the gas leaving the scrubbers be made simultaneously.

Volume of Coke-Oven Gas Required for Charcoal Absorption Method

Gal. Light Oil per Ton Coal (12,000 Cu. Ft.)	Cu. Ft. Gas Required for Determination
0.5	190–250
1.0	95–125
1.5	63–83
2.0	47–60
2.5	38–50
3.0	31–41
3.5	27–36
4.0	24–31
4.5	21–28

The spent activated carbon containing cresol may be revivified, but it is more satisfactory to use fresh material for each determination.

STARCH AND STARCH PRODUCTS

Starch is used in the paper industry for four purposes: (1) Engine sizing; (2) tub sizing; (3) pasting, and (4) coating. It is necessary to divide it into two main classes, with a method of analysis for each class. The first to be known as raw starch and to include all starches which have not been treated in any other way than by the purifying methods used in their manufacture. The second to be known as converted starches with subclasses. The method of sampling for all kinds of starch products to be the same, and to be embodied as part of the method of analysis.

Sampling.—Ten bags or barrels are taken from different parts of a car. These are sampled by means of a 1-inch tryer 12 inches long. One filing of the tryer is to be taken from each bag or barrel. Samples so obtained are mixed, bottled and sealed in three jars, one for each party to the transaction, and one for reference. For smaller deliveries than a carload 10% at least of the bags or barrels should be sampled.

Preliminary Examination.—Raw Starch: (*a*) Spread out 100 grams of the sample on a sheet of white glazed paper, and examine for foreign material.

(*b*) Mix this sample with 500 ml. of water to a smooth cream and strain through a 200-mesh silk bolting cloth. Compare residue on silk with standard sample of the same grade, treated in the same manner, at the same time.

(*c*) Stir filtrate from above for two seconds with a circular motion, and let stand thirty seconds. Decant carefully, and compare residue with a standard sample of the same grade of starch, treated in the same manner, at the same time.

Moisture.—Dry approximately 5 grams to constant weight at 100° C. Loss in weight is calculated as moisture.

Ash.—Weigh out 1 gram of the sample; transfer to a platinum crucible; ignite to constant weight.

Acidity.—Weigh out 20 grams on a watchglass. Transfer to a 250-ml. porcelain dish. Add approximately 200 ml. of water, and stir until starch forms a smooth cream. Titrate with N/10 caustic soda, using phenolphthalein as indicator until a faint pink color persists for twenty seconds.

Alkalinity.—Method is same as for acidity, except that sample should be titrated with N/10 sulfuric acid until the pink coloration just disappears.

Test for the Presence of Alkaline Starch or Alkali.—Add a few drops of phenolphthalein solution to water in a white porcelain dish; sprinkle in a little of the dry sample. If some of the grains turn pink, it indicates that the sample is a mixture of raw starch and alkaline starch or alkali. If all the particles turn pink, the material is an alkaline finished starch.

Viscosity.—Take 12 grams of the sample in 300 ml. of water, bring to boil, then boil for ten minutes with constant stirring in an aluminum beaker over a naked flame. Determine viscosity at 100° C. with 200 ml. of the liquid in a Scott viscosimeter, standardized as follows: Calibrate to hold 200 ml. of water at 100° C. Determine viscosity on first 50 ml. withdrawn. Express result as a ratio. (Starch viscosity) ÷ (water viscosity) = viscosity number.

Converted Starches.—Owing to the number and variety of the products on the market, their classification is a matter of some difficulty. The method of conversion, however, may be used as a means, and thus the following classes can be arranged: (1) Thin boiling starch, mainly used for tub sizing, converted by treatment with weak acid solutions by the " in suspension " or " drying in " process. (2) Partly dextrinized starches, and dextrins, made by damping the starch with small quantities of acid, and converting at a high temperature by the dry process. (3) Oxidized starches. (4) Acetylated starches. (5) Alkali-treated starches, including products consisting of raw starch mixed with certain quantities of various alkalies and alkaline salts. (6) Mixtures of starch products and mineral fillers. (7) Mixture of starch products with glue and casein or other sizing agents. (8) Products in solution or paste form.

Sampling, Moisture and Ash are the same as for raw starch.

Acidity and Alkalinity.—First method same as for raw starch.

Total Acidity.—Mix 10 grams of the sample in 200 ml. of water and heat on a water bath for five minutes after reaching 75° C.; cool and titrate. This gives the acidity within the starch granule.

Viscosity.—In determining viscosity the starches are divided into three classes: (*a*) Low boiling, or laundry starch; (*b*) medium thin boiling; (*c*) high thin boiling, with a decrease in viscosity from (*a*) to (*c*). For (*a*) the viscosity should be determined in a 10% solution; for (*b*) in a 20% solution; for (*c*) in a 30% solution. Otherwise the method is the same as for raw starch.

Added Materials.—These are tested for by the ordinary methods used in separating and identifying mineral fillers, metallic salts, glue, casein, and other

vegetable sizes. The identification of the product in relation to the classification of the process of manufacture involves a more exhaustive analysis including: (1) The identification of the starch by microscopical observation. (2) Combined acid to determine the degree of acetylation of the product. (3) Solubility in cold water and reaction with Fehling's solution, which gives a measure of the degree to which the starch has been hydrolyzed and dextrinized. (4) Color reaction with iodine and other agents. (5) *Technical Valuation*—Character of Size. A sample of the starch product is mixed with four or five times its weight of water, and heated on a water bath, for at least twenty minutes after swelling.

(*a*) Portions of the size are allowed to cool, and the time of setting observed. This gives a figure for the permanency of the solution.

(*b*) A little of the size is rubbed out on paper and allowed to dry, when the surface and finish produced is observed.

(*c*) The solution is run out on a clean glass plate to a thin layer and allowed to dry at room temperature. Film produced is examined and compared with, say, a gelatin film, for physical characters.

Sizing Strength.—For paper coating the size is prepared under the proper conditions for the particular product and mixed with definite quantities of clay or other filler. A series of samples is made up at graduated strengths according to the proportions used in practice, and samples of paper are coated by color obtained. The sizing power of the sample is determined, in comparison with other sizing materials, treated in the same manner, at the same time, by noting the resistance to spirit varnish, or by using the sealing wax test and others. In most cases, both for coating and tub sizing, the most accurate and reliable results are only obtainable by a working trial under standard conditions.

TANNIC ACID [12]

The following procedure is applicable for the examination of pure tannic acid solutions and tannins.

Reagents

Potassium Permanganate.—Approximately N/10 $KMnO_4$. Standardize against N/10 oxalic acid solution.

Indigo Carmin Solution.—5 grams of pure indigo carmin dissolved in water, 50 grams of conc. H_2SO_4 are added and the solution diluted to 1000 ml.

[12] References: H. R. Proctor, "Leather Industries Laboratory Book of Analytical and Experimental Methods."
Knecht-Rawson-Lowenthal, "Manual of Dyeing," Vol. II, pp. 802, Eighth Edition.
Leach, "Food Inspection and Analysis," p. 282.

Gelatin Solution.—20 grams of pure gelatin dissolved in hot water and diluted to 1 liter.

Saturated NaCl Acid Solution.—5% H_2SO_4 solution saturated with NaCl.

Total Astringency—Lowenthal-Proctor Method

Standardization of the Indigo Carmin Solution.—The filtered solution should give a yellow color free from brown when oxidized with $KMnO_4$.

Twenty-five ml. of the reagent in a porcelain casserole are diluted to 750 ml. with water and the $KMnO_4$ reagent added drop by drop from a burette with constant stirring until a pure yellow color is obtained. The rate of titration should be uniform in all tests and should be carried out very cautiously as the endpoint is approached. This is recognized by a faint pinkish rim appearing, best seen on the shaded side of the casserole.

Procedure for Astringency.—1 gram of solid (or 2–5 grams of solution sumac extract) is dissolved in water and diluted to 1 liter. 10 ml. of this solution is placed in a large casserole containing 750 ml. of water. 25 ml. of the carmin solution are added and the mixture titrated with N/10 $KMnO_4$ as described for standardization of the indigo carmin reagent. From this titration the number of ml. $KMnO_4$ required by 25 ml. of indigo carmin reagent are subtracted and the difference represents the $KMnO_4$ required by the sample. Multiply ml. $KMnO_4$ required by sample by $0.004157 = A$.

Astringent Non-tannins.—To 50 ml. of the solution (in an 8 oz. bottle) made as stated in the previous determination are added 25 ml. of 2% gelatin solution and 25 ml. of the saturated NaCl acid reagent followed by 10 grams of china clay. The bottle is stoppered and the mixture shaken for five minutes and then filtered through a dry filter, thus removing the tannins. The filtrate is tested with more gelatin solution to see that the tannin is completely precipitated. (A stronger gelatin solution should be used if tanning is evident and the test repeated with 25 ml. of this.) 20 ml. of the filtrate, equivalent to 10 ml. of the original solution, are titrated with N/10 $KMnO_4$ exactly as in the preceding test and the ml. $KMnO_4$ consumed by the non-tannins is multiplied by the value of the $KMnO_4$ ($N/10 = 0.004157$) and the result recorded as B.

Tannic Acid or Tannins.—The difference between the total astringency, calculated as tannin, and the astringent non-tannins gives the amount of tannins, namely result A minus result B = grams tannin. Calculate to percentage.

1 ml. N/10 $KMnO_4 = 0.004157$ gram tannin.

BLEACHING POWDER

Sampling.—Twenty per cent of the packages in the shipment should be sampled. The sample shall be taken by boring or cutting a two-inch hole through the side of the wooden cask or iron drum midway from the ends, or through the head near the center. The sampler, which consists of a stout iron scoop about one and a half inches wide and eighteen inches long, shall be inserted for two or three inches, withdrawn, and the bleach removed discarded. The sampler shall be inserted again as far as it will go, removed, the bleach

transferred to a glass fruit jar, and the jar closed until the next cask is sampled. The portions from the several casks shall all be mixed together to make one composite sample representing the shipment.

Available Chlorine.—Ten grams of bleaching powder from the well-mixed sample is weighed out and triturated in a mortar, adding small quantities of distilled water at a time and grinding thoroughly after each addition until the powder is converted to a voluminous paste free from dense particles. The liquor after each trituration is poured off into a 1000-ml. graduated volumetric flask, and the paste is finally washed into flask. Fill the flask to the mark with distilled water, shake well and draw off an aliquot portion by means of a 50-ml. pipette for analysis, observing the precaution that the liquor drawn off contains its proportion of suspended matter. The available chlorine is determined by titration with N/10 sodium arsenite solution, using starch iodide paper as an indicator.

NOTE.—The N/10 sodium arsenite solution is made by drying arsenic trioxide, which answers Krauch's requirements for purity, in a desiccator over night, 4.95 grams being weighed out and dissolved in 200 ml. distilled water with 20 grams of pure sodium carbonate, the solution cooled and made up to 1 liter, then standardized with resublimed iodine.

One gram of potato starch is mixed with distilled water to a cream and then poured slowly into 100 ml. of boiling water and the liquid allowed to boil gently for two minutes when 1 gram of c.p. potassium iodide, dissolved in a little distilled water, is poured in. The liquid is then thoroughly mixed, allowed to settle and strips of unsized paper are soaked in the solution and hung up to dry, out of contact of fumes.

Chlorates.—The solution in which the available chlorine has been determined by means of N/10 sodium arsenite is slightly acidified with sulfuric acid, the solution transferred to a narrow-mouth flask, and a quantity of pure ammonium ferrous sulfate is added in excess of that required to reduce all chlorates to chlorides. The flask is then stoppered with a 2-hole rubber stopper, which is fitted with a small separatory funnel through one opening, and a small glass tube ending in a short piece of rubber tubing (which may be clamped tight when needed) is fixed in the other opening. The liquid is then brought to boiling and 15 ml. of 1.29* sulfuric acid is added drop by drop, through the funnel. When acid is all in, close opening in funnel and clamp rubber tubing on vent, cool, and titrate back the excess of ferrous ammonium sulfate with N/10 potassium permanganate.

Total Chlorides.—The slight pink color produced by the permanganate is removed by the addition of a drop or two of N/10 ferrous ammonium sulfate, and an excess of N/10 silver nitrate solution is added.

The silver chloride is filtered off, washed well and the excess silver nitrate is determined by means of N/10 potassium thiocyanate, the iron in solution acting as an indicator. See chapter on Chlorine, Vol. I.

NOTE.—The chlorine as chlorates plus the available chlorine subtracted from the total chlorine as chlorides gives the chlorine present originally in the bleach as chlorides.

Determination of Bases and Silica.—To 2 grams of bleaching powder add 25 ml. 1.12* HCl and 50 ml. of 3% H_2O_2. Digest and evaporate on steam bath

* Specific gravity.

or hot plate. Dehydrate the silica and determine the silica, alumina, iron, calcium oxide, and magnesia as in lime analysis.

Free Lime.—To 100 ml. of bleach liquor made up for the available chlorine determination add 25 ml. hydrogen peroxide, bring to boil and oxidize the hypochlorite. The solution is then titrated with standard acid. At the same time the acidity of the H_2O_2 used should be determined and a correction made for the amount used in destroying the hypochlorite. The free lime is calculated from the acid consumption.

Quality of Powder for Producing Bleach Liquor.—Sixty grams of bleaching powder is weighed out and added to 1000 ml. distilled water in a glass jar $4\frac{1}{2}$ inches in diameter and 5 inches deep. The mixture is stirred vigorously by means of a glass rod bent so that it just clears the bottom and sides of the jar, driven by power from electric or water motor at 250 r.p.m. for exactly 15 minutes. The jar is then placed on a bench free from vibration and the time required for the dregs to settle to the bottom noted; 25 ml. of the clear bleach liquor is then measured out and tested in the usual way for available chlorine.

Determination of Wood and Coarse Impurities.—100 grams of the powder is triturated in a porcelain mortar, washed through a 60-mesh sieve, residue is dried and weighed.

Proximate Analysis for Sand and Grit.—To 10 grams of the powder add 75 ml. of 1.12 hydrochloric acid, and warm until all lime salts are dissolved, dilute to 200 ml. with distilled water, pour off the supernatant liquid, again dilute to 200 ml. with distilled water, filter, wash, and ignite the residue.

NOTE.—If preferred, a potassium iodide-starch solution preserved with a drop of CCl_4 or CS_2 may be used as the indicator in the determination of available chlorine by testing a drop of the bleach liquor with a drop of the indicator on a pill tile rather than the use of the potassium iodide-starch paper. If desired, soluble starch, which dissolves readily in hot water, may be used in the preparation of this indicator.

ANALYSIS OF CLAY [13]

Chemical Analysis.—The sample should be finely ground, if necessary a large quantity, 2 to 10 pounds, should be weighed and dried on steam table, weighed again and loss in moisture calculated to percentage; it may then be finely ground.

A weighed quantity, 1 to 10 grams, should now be dried at 100° C. to constant weight, this loss calculated to percentage and added to that from the first drying and is the moisture. A weighed portion, 1 to 2 grams, of the moisture-free powder is heated, in a covered crucible, to bright redness for 10 minutes, cooled and reweighed; loss = combined water and organic matter. Or a weighed quantity is put in a boat which is heated in a tube in a current

[13] By J. M. Wilson, Lefax, 9–196, June, 1919. By courtesy of Lefax, Philadelphia.

of dry air and drawn through a weighed $CaCl_2$ tube; gain in weight = combined moisture.

Mix 1 gram dry clay with 5 g. $Na_2CO_3 + \frac{1}{2}$ g. KNO_3 in a platinum crucible, fuse 30 to 40 minutes, cool, detach melt from crucible. Wash crucible with H_2O, then HCl, then H_2O, pouring all washings into a porcelain dish, and add the melt. Cover dish, add HCl little at a time until in considerable excess. Evaporate dry, bake 1 hour at 120° C. Cool, moisten well with HCl. Evaporate and bake again. Cool, moisten HCl, take up in H_2O, boil 10 minutes, filter, wash with hot HCl (1 : 1), cold H_2O, hot HCl, cold H_2O, then 5 to 6 times hot H_2O, ignite in a weighed platinum crucible and hold.

Evaporate the filtrate and washing in a dish, bake as above, moisten with HCl, evaporate and bake again. Take up HCl + H_2O filter and wash as above. Burn this filter in same crucible, cool, weigh = crude SiO_2. Moisten with few drops H_2SO_4 (1 : 4), then H_2O to make a thin mud; add enough HF to fill crucible $\frac{2}{3}$ full, evaporate at gentle heat; heat cautiously over lamp—to avoid spattering—raising heat slowly to full heat of lamp. Loss in weight = SiO_2.

If any residue remains in the crucible, fuse with $KHSO_4$. Leach melt with H_2O and add to main filtrate.

Boil filtrate from silica, add 1 to 3 ml. HNO_3, boil 10 minutes. Add NH_4OH in slight excess, boil 3 minutes, let settle in warm place, decant through a filter. Add hot water to precipitate, stir, let settle, filter, dissolve precipitate in HCl (1 : 1). Dilute to 250 ml., boil, reprecipitate as above, repeat again, wash thoroughly with hot H_2O. Ignite and weigh precipitate = $Fe_2O_3Al_2O_3$-($P_2O_5 \cdot TiO_2$).

Fuse with $KHSO_4$, leach with H_2O, reduce in Jones reductor. Titrate Fe with $KMnO_4$. $Fe/0.7 = Fe_2O_3$.

Fuse 2 to 5 grams dry sample with 5 wts. $Na_2CO_3 + \frac{1}{2}$ wt. KNO_3. Leach melt with H_2O, filter, wash with $H_2O + Na_2CO_3$. Save residue for Ti. Acidify filtrate with HNO_3, boil off CO_2, add Fe_2Cl_6 solution (free from Phos.), boil. Add NH_4OH, filter, take up precipitate in HNO_3. Boil well and precipitate the phosphorus with ammonium molybdate. Determine phosphorus.

$$P \times 2.29 = P_2O_5.$$

$$(Al_2O_3 + Fe_2O_3 + P_2O_5 + TiO_2) - (Fe_2O_3 + P_2O_5 + TiO_2) = Al_2O_3.$$

Evaporate united filtrates from Al_2O_3, etc., to 100 ml. Make ammoniacal, add Br_2 in excess, then 60 to 70 ml. NH_4OH, boil 20 minutes, filter, wash with hot H_2O. Ignite and weigh Mn_3O_4. $Mn_3O_4 \times 0.93006 = MnO$.

Acidify filtrate from MnO_2, evaporate dry, take up in HCl + H_2O (volume 150 ml.), boil, add NH_4OH till neutral, then ammonium oxalate. Boil 10 minutes, cool 2 hours, decant close as possible through filter. Dissolve precipitate in HCl, dilute to 100 ml., add ammonium oxalate, boil. Precipitate with NH_4OH, boil 10 minutes, filter after 2 hours, wash twice with cold H_2O, then 5 or 6 times with hot H_2O. Ignite strongly, weigh while still warm, repeat ignition and weighing = CaO. Or dissolve precipitate in least quantity HCl (1 : 1) through filter into an Erlenmeyer flask. Wash with H_2O, add 25 ml. H_2SO_4 (1 : 4), heat to 80° C., titrate with $KMnO_4$. Fe value $KMnO_4/2 = CaO$.

Evaporate combined filtrates from CaO to small volume (15 to 20 ml.), add 1 gram ammonium phosphate $(NH_4)_2HPO_4$, then NH_4OH till solution is neutral. Cool under tap, stir till precipitate forms, set aside 15 minutes,

stirring occasionally. Add ½ volume NH_4OH, stir, let stand 4 hours, filter but do not wash. Dissolve through filter in HCl into vessel in which precipitation was conducted. Wash filter with H_2O, reprecipitate with NH_4OH as before, filter on weighed Gooch felt. Wash with (NH_4NO_3, 60 g.; H_2O, 80 ml.; NH_4OH (1 : 3), to 600 ml.), dry at 100° C., ignite carefully till a glow passes over the precipitate, cool and weigh $Mg_2P_2O_7$.

$$Mg_2P_2O_7 \times 0.36207 = MgO.$$

Alkalies.—Weigh 1 gram clay, 1 gram NH_4Cl into a platinum crucible, mix thoroughly. Add 6 grams $CaCO_3$ (free from alkalies), mix, cover with 2 grams $CaCO_3$. Heat covered crucible very gently till no more fumes are given off. Raise heat slowly till lower third of crucible is at good red heat. Maintain this heat for 15 minutes, cool, transfer sintered mass to a porcelain dish. Wash out crucible with water into dish, add more water till volume is 200–300 ml. Digest at 100° C., breaking lumps with a glass rod, then boil 5 to 10 minutes, add $(NH_4)_2CO_3$, allow to stand 20 to 30 minutes. Filter into a porcelain dish, wash thoroughly with hot H_2O containing $(NH_4)_2CO_3$. Evaporate nearly dry, add NH_4OH + ammonium oxalate, filter into a platinum dish. Evaporate dry, ignite gently to drive off ammonium salts, cool, add $(NH_4)_2CO_3$ + ammonium oxalate, filter through very small filter into a weighed platinum dish. Evaporate dry, ignite gently till ammonium salts are volatilized, raise heat till bottom of dish is a faint red, cool and weigh. Moisten with a drop or two of HCl, heat again and weigh = NaCl + KCl. Separate 1st by $PtCl_4$, 2d by perchloric acid, 3d by titration of Cl with $AgNO_3$, or 4th by conversion into sulfates and determining the SO_3 with $BaCl_2$.

Titanium.—Decomposition, (1) by fusion with 5 wts. Na_2CO_3 + ½ wt. KNO_3, leaching with H_2O, and extracting TiO_2 from residue, (2) by fusion with $KHSO_4$, leaching with $H_2O + H_2SO_4$, filtering and precipitating TiO_2 from filtrate, (3) by moistening with dilute H_2SO_4 and evaporating with HF to remove SiO_2 and decompose silicates.

Precipitate, add NH_4OH to solution until a faint precipitate is produced, then HCl to redissolve the precipitate and leave a slight excess. Dilute to 250 ml., add strong solution $Na_2S_2O_3$ and boil 20 minutes. Let settle, decant through a filter, wash once by decantation, keeping as much of the precipitate in the beaker as possible. When filter has drained, place beaker, in which the precipitation was made, under the funnel and treat filter with concentrated HCl. Allow to act 15 to 20 minutes, wash filter thoroughly with cold H_2O, repeat the precipitation as above, filter, wash well with hot H_2O, ignite and weigh TiO_2.

When TiO_2 is present in small amount, it may be determined by color. Standard $Ti(SO_4)_2$ solution is made as follows: Fuse ½ gram rutile with Na_2CO_3, leach melt with H_2O, filter, take up insoluble in H_2SO_4 (1 : 4), evaporate to fumes, cool, take up with $H_2O + H_2SO_4$, filter if necessary, dilute till 1 ml. = 0.001 gram Ti. Decompose clay by fusion with Na_2CO_3 and treat the residue with H_2SO_4. Evaporate to fumes, take up with $H_2O + H_2SO_4$, pour into a Nessler tube. Fill another Nessler tube nearly to same volume with H_2O. To each add 5 ml. H_2O_2 and to the standard add the standard $Ti(SO_4)_2$ from a burette until the brown colors match, when the volumes are equal. The

burette reading will then give the number of milligrams of Ti in the clay from which the percentage may be calculated.

State of Silica.—*A*—Combined with bases in the clay, *B*—Hydrated silica, *C*—Sand or silicates. Moisten 2 grams dry powder with H_2O, add 20 ml. H_2SO_4 (conc.), cover dish, heat 10 hours, remove cover, evaporate dry, cool, take up in H_2O, filter, wash with H_2O, ignite and weigh $= A + B + C$.

Boil with Na_2CO_3 solution, allow to settle, decant through a weighed Gooch felt or alundum crucible, repeat boiling and decantation until a portion of the filtrate gives no precipitate with NH_4Cl on standing. Transfer residue to filter and wash thoroughly with hot H_2O, acid, then hot H_2O. Ignite and weigh $= C$. A and B are in filtrate.

Boil 4 to 5 grams dry powder with strong solution of Na_2CO_3, filter, wash with hot H_2O. Acidify filtrate with HCl, evaporate dry, bake at 120° C., cool, moisten with HCl, evaporate dry, bake again. Take up in HCl and H_2O, filter, wash, ignite; weigh as $SiO_2 = B$. $(A + B + C) - (B + C) = A$.

If $A + B + C =$ total SiO_2 found on analysis, C is quartz. If $A + B + C$ is greater than total SiO_2, C is in form of silicate and weight of SiO_2 as silicates $= A + B + C -$ total SiO_2 found in 1 gram.

ANALYSIS OF GLASS [14]

As glass consists of such a variety of substances, to define it exactly is a decidedly perplexing problem. Neither can a formula be written for such a substance, because it may contain many different radicals, and also because glass is a mixture of silicates and not a definite compound.

It is also quite a problem to write up an analysis of glass that will embrace all glasses. The most common substances usually found in clear glasses are Silica, Lead, Alumina, Calcium, Magnesia, Soda, Potash, Iron as an impurity, and other substances found in special glasses and colored glasses such as Barium, Borax, Manganese, Sulfur, Zinc, Tin, Copper, Chromium, Gold, and Uranium, Fluorides, Phosphates, Lithium and Strontium are also occasionally found. Antimony, Arsenic, Cobalt, Selenium, Titanium, etc., are not uncommon but are usually present in such small quantities that they are seldom determined or even looked for.

In the following analysis only the substances most frequently encountered by the glass chemist will be considered. They are—Silica, Lead, Iron, Alumina, Calcium, Magnesia, Soda, Potash, Barium, Borax, Manganese and Sulfur. If an unknown glass is to be analyzed, it is always necessary to make a qualitative examination of the sample before any quantitative work should be attempted.

[14] By G. E. Fisher, Lefax, 11–319. By courtesy of J. C. Parker, President Lefax, Philadelphia.

Density or Specific Gravity.—The value and importance of knowing the specific gravity of a glass is quite often overlooked but its value becomes more evident as one continues to make the determinations and link them up with the analysis of the glass in question. It is always advantageous to take the specific gravity before the glass is analyzed as it quite often gives a clue as to the type of glass, especially to the person who is familiar with linking gravity and analysis. It is always interesting to calculate the specific gravity from the percentages of constituents in the analysis. This can be done by any who have the proper tables and formula at hand.

The specific gravity of a piece of glass weighing as little as 8 grams can be very accurately determined on the analytical balance. By making substitution in the equation:

$$D = \frac{W_1 - W_2}{W_1},$$

where D = specific gravity, W_1 = weight in air, W_2 = weight in water, the density is easily computed. Duplicate computations should check within five points in the third decimal place.

Preparation of Sample and the Determination of Silica.—Grind the sample of glass to an impalpable flour with a mortar and pestle. Weigh out 1 gram of the finely powdered glass into a platinum crucible. Weigh out 4 grams of sodium potassium carbonate fusion mixture and about half a gram of potassium chlorate and transfer to the same crucible. Mix thoroughly and take care not to lose any. Fuse this and keep it hot till the mass is a liquid in the bottom of the crucible. Allow the mass to cool off considerably and then take up the melt with 50 to 100 ml. of hot water containing about 10 ml. of hydrochloric acid. If borates are present, refer to the removal of borates under "Determination of B_2O_3." Transfer to an evaporating dish and evaporate to dryness on a steam bath and then bake for at least half an hour on a hot plate at 110° C. Then take up with dilute hydrochloric acid and water and filter. Wash the residue with hot water until free from chlorides. Save this residue. Transfer the filtrate to the evaporating dish and evaporate and bake as before. Take this up with water and hydrochloric acid and filter and wash with hot water until free from chlorides. Combine this residue with the first one and ignite to constant weight in a previously ignited platinum crucible. After weighing, moisten with *dilute* sulfuric acid and then fill the crucible three quarters full with hydrofluoric acid and evaporate to dryness in an iron cone, ignite and weigh. Deduct the weight of this residue from that of the above weighing. The difference in weights is the weight for corrected silica from which the percentage is easily calculated. Fuse the residue which remains in the crucible with about 2 grams of potassium bisulfate, take up with dilute hydrochloric acid and add it to the main solution. If the sodium potassium carbonate fusion mixture is not known to be pure, it should be analyzed and corrections made accordingly.

Determination of PbO.—Neutralize the solution, then make it just acid with 1 drop of hydrochloric acid. Pass in hydrogen sulfide gas for several minutes to insure complete precipitation. Allow the lead sulfide to settle, then filter on a Gooch crucible. Wash the residue with water saturated with hydrogen sulfide. Again pass hydrogen sulfide into this filtrate to be sure

precipitation is complete. Preserve the filtrate for the estimation of iron, etc. Dissolve the lead sulfide in dilute nitric acid (1 : 4). Filter this solution to remove the asbestos used in the Gooch. Precipitate lead sulfate from this solution by adding dilute sulfuric acid with constant stirring. Then add 100% by volume of 98% ethyl alcohol to the *cold* solution. Allow the precipitate to settle for an hour and filter on a weighed Gooch previously ignited at a red heat. Wash with 50% alcohol. Heat the residue slowly and ignite at a dull red heat until the residue is white. Cool and weigh as lead sulfate. Calculate the percentage of PbO by using the proper factors which may be found in the table below.

Determination of Fe_2O_3 and Al_2O_3(R_2O_3).—Boil this solution with 2 or 3 ml. of nitric acid to remove the sulfur and oxidize the iron. Cool the solution. Add about 5 grams of ammonium chloride and then add ammonium hydroxide until the solution is slightly ammoniacal. Boil cautiously for about 5 minutes. Allow the precipitate to settle. Filter and wash with hot water or hot 2% ammonium nitrate solution. Preserve this filtrate for the determination of calcium. Ignite the residue in a weighed platinum crucible. Cool and weigh as Fe_2O_3 and Al_2O_3. Fuse this residue with potassium bisulfate and digest with dilute sulfuric acid. Transfer to a 250-ml. Erlenmeyer flask. Pass in hydrogen sulfide gas to reduce the iron. Then fit a Bunsen valve to the flask and boil to a small volume to drive off the excess hydrogen sulfide. Cool and add a pinch of sodium bicarbonate and titrate with standard N/200 potassium permanganate solution. From the amount of standard solution used calculate the percentage of iron oxide. Deduct the percentage of iron oxide from ($Fe_2O_3+Al_2O_3$) and the difference is the per cent Al_2O_3.

Determination of CaO.—Bring the solution to boiling. While hot add 10 to 20 ml. of hot saturated ammonium oxalate solution with constant stirring. Then add about 5 ml. of ammonium hydroxide. Allow to stand for several hours or preferably over night. Filter off the calcium oxalate and wash with a 2% ammonia water. Preserve the filtrate for the determination of magnesia. Ignite the residue at full blast in a previously ignited and weighed platinum crucible to constant weight. Weigh as calcium oxide.

Determination of MgO.—Concentrate the solution by boiling and while hot add 10 to 20 ml. of saturated microcosmic salt solution with constant stirring. Then add ammonia and stir vigorously, taking care not to strike the sides of the beaker. Allow the precipitate to settle for several hours or preferably over night. Filter and wash with a 2% solution of ammonia water. Dry the residue and filter paper. Ignite slowly at first and then at full heat in a weighed porcelain or platinum crucible, until constant weight. Cool and weigh up as magnesium pyrophosphate. Calculate the percentage of MgO by using the factor found in the table below. If large amounts are to be ignited, it is best to ignite the residue and paper separately in a porcelain crucible.

Determination of the Alkalies.—The method in general use is that of Sullivan and Taylor. Weigh out 1 gram of finely powdered glass in a platinum crucible of about 40 ml. capacity, moisten with water and add 2 grams of oxalic acid crystals and enough 48% hydrofluoric acid to fill the crucible half full. This is evaporated to dryness and warmed to a temperature which is just high enough to expel the excess oxalic acid. When all the acid is expelled, the crucible is cooled and the evaporation repeated twice more with oxalic acid and water.

The amount of oxalic acid used is about 5 grams in all. After the third evaporation when all the excess of oxalic acid is expelled, the remaining oxalates are taken up with hot water, allowed to cool and filtered. The residue which consists of lead oxalate and calcium oxalate is filtered off. The filtrate is evaporated to dryness in a platinum dish and then heated over a free flame until oxalates are decomposed to carbonates. The insoluble carbonates are filtered off and the alkali carbonates are in the filtrate. The filtrate is made acid with hydrochloric and evaporated to dryness to remove traces of silica. The filtrate is evaporated to dryness in a platinum dish, the sodium chloride and potassium chloride heated to incipient fusion, cooled and weighed. This gives the weight of the combined alkali chlorides. The chlorides are dissolved in about 25 ml. of water and 4–5 ml. of chloroplatinic acid (1 gram Pt in 10 ml.) added and the solution evaporated to a syrupy consistency. The insoluble potassium chloroplatinate is filtered on a Gooch. Wash by decantation with 85% ethyl alcohol until the washings are colorless. The Gooch is dried at 130° C. to constant weight. The potassium chloroplatinate is computed to potassium chloride, and the sodium chloride found by difference from the weight of the combined alkali chlorides. Both potassium chloride and sodium chloride are computed to their respective oxides.

Determination of B_2O_3.—Before proceeding with any of the determinations, boric acid must be removed. This is done by adding 25 ml. of methyl alcohol in both dehydrations of silica. Then proceed as usual. The determination of B_2O_3 must be made as follows on a separate sample of glass. Fuse .5 gram sample with about 4 grams of sodium carbonate. Take up with 20–30 ml. dilute hydrochloric acid and add a few drops of nitric acid to oxidize the iron. Place the whole in a 250 ml. round bottom flask. Heat nearly to boiling and add dry precipitated calcium carbonate in moderate excess. * Connect with a reflux condenser and boil vigorously for ten minutes to remove CO_2 from the solution. Filter off precipitate through a small Büchner funnel, washing several times with hot water. Keep the volume below 100 ml. Return the filtrate to the flask and add a small amount of calcium carbonate and again heat to boiling. Connect up to a filter pump, through a splash trap, and continue suction cautiously, until boiling has nearly ceased, to remove the last traces of CO_2 in the solution. Cool to room temperature and filter if necessary. Add 4–5 drops of phenolphthalein indicator and run in slowly N/10 standard sodium hydroxide solution until the liquid is decidedly pink. Add about 1 gram of mannite or 10 ml. glycerol and shake. The pink color will disappear. Then run in more standard NaOH till pink and then more glycerol. Continue this until the pink is permanent. The glycerol must be neutral. The standard NaOH should be standardized against a standard sample of B_2O_3. The percentage B_2O_3 can then be computed.

This method is unsatisfactory when zinc and lead are present in the glass as high results are obtained. Fuse a half-gram sample with 4 grams of sodium carbonate. Digest with 20–30 ml. of hot water and when the melt is entirely decomposed filter off any insoluble oxides. After washing, transfer the filtrate to a 250-ml. round bottom flask. Add about 7 ml. concentrated hydrochloric acid. Heat nearly to boiling and add a moderate amount of calcium carbonate in excess; from here proceed as above from asterisk.*

Determination of MnO_2.—The iron and alumina precipitation with ammonia also effects the precipitation of manganese. It is then necessary to separate these three substances. The residue containing Fe_2O_3, Al_2O_3, MnO_2 is dissolved in dilute nitric acid. It is necessary that the solution be free from ferrous iron. To this solution add as much sodium carbonate as possible without any precipitation taking place. This must be added very cautiously drop by drop. Dilute and add one-half gram of sodium acetate and boil. Let settle and filter. Wash with a $\frac{1}{2}\%$ solution of ammonium acetate. The filtrate should now be neutral to methyl orange. The residue contains the iron and alumina. The filtrate contains the manganese. Dissolve the residue in dilute hydrochloric acid and determine iron and alumina by the foregoing method. The filtrate should be concentrated. Add 10 grams of sodium acetate. The solution should now have a volume of about 200 ml. Bromine water is then added until the color is distinct. The solution is then boiled for about 15 minutes, with small additions of bromine water. The precipitate is then allowed to settle. Filter and wash. Dissolve the residue in hot dilute hydrochloric acid containing a little bisulfite. Add ammonium phosphate, then ammonia slowly, with heating and constant stirring. Allow it to settle a few hours, then filter and wash with a dilute solution of ammonia water. Ignite in a weighed porcelain crucible, as manganese pyrophosphate, and compute the percentage of MnO_2 from the factor in the table below.

Determination of Sulfur.—A separate sample should be used for the estimation of sulfur. Weigh out a 2 gram sample, mix with 5 grams of sodium potassium carbonate fusion mixture and a half gram of potassium nitrate. During fusion the charge should be protected from the flame by an asbestos board provided with a hole to accommodate the crucible. Take up the fusion with water, transfer to an evaporating dish and dehydrate. Take up with dilute hydrochloric acid, filter and wash. Dehydrate the filtrate the second time, take up with dilute hydrochloric acid, boil to drive off carbon dioxide, filter and wash. To the hot filtrate add enough barium chloride solution to precipitate the sulfur completely. The barium chloride should be added very slowly and with constant stirring. Allow the barium sulfate to settle several hours and then filter on a weighed ignited Gooch. Wash with a dilute alcohol solution. Ignite at a temperature of about 800° C. Cool and weigh as barium sulfate. Compute percentages from the table given below.

Determination of BaO and Separation of Barium from Calcium.—This separation is made from the solution from which iron and alumina have been precipitated. Boil this solution sufficiently to remove the ammonia. Evaporate the filtrate nearly to dryness. Then take up with about 300 ml. of water and add 5–6 drops of acetic acid with enough ammonium acetate to neutralize any free mineral acid present. Heat the solution and add an excess of ammonium chromate. Allow the barium chromate precipitate to settle for an hour or more. Filter on a weighed Gooch and wash with water containing ammonium chromate, until free from calcium. Then wash with water until free from ammonium chromate. Dry the precipitate at 110° C. and ignite gently at first and finally to a dull red heat. Weigh as barium chromate and compute the percentage of BaO from table.

TABLE OF COMPUTATION FACTORS

$BaSO_4$	$\times 0.1373 = S$	$PbSO_4$	$\times 0.736 = PbO$
	$\times 0.2744 = SO_4$		$\times 0.683 = Pb$
	$\times 0.3430 = SO_3$	$Mg_2P_2O_7$	$\times 0.218 = Mg$
	$\times 0.4115 = SO_4$		$\times 0.362 = MgO$
	$\times 0.4202 = H_2SO_4$	$Mn_2P_2O_7$	$\times 0.387 = Mn$
	$\times 0.821 = Na_2SO_4$		$\times 0.612 = MnO_2$
	$\times 0.747 = K_2SO_4$	K_2PtCl_6	$\times 0.306 = KCl$
	$\times 0.892 = BaCl_2$		$\times 0.193 = K_2O$
$BaCrO_4$	$\times 0.541 = Ba$	KCl	$\times 0.631 = K_2O$
	$\times 0.605 = BaO$	$NaCl$	$\times 0.530 = Na_2O$

ANALYSIS OF THE MOST IMPORTANT GLASS-MAKING MATERIALS [15]

Potash (Potassium Carbonate) Water Insoluble. Dissolve five grams of the sample in 100 ml. of distilled water and filter off any insoluble matter on a tared Gooch crucible. Dry, cool and weigh.

Moisture.—Weigh out a five gram sample into a tared porcelain crucible or a small evaporating dish and heat in an electric oven at 110° C. for several hours. Cool and weigh and report the loss in weight as moisture.

Chlorides.—Dissolve a five gram sample in 100 ml. of distilled water. Filter if necessary. To the filtrate add a few ml. of nitric acid until the solution is acid and then add silver nitrate solution until precipitation of the chlorides is complete. Heat the solution to boiling and stir vigorously to coagulate the silver chloride. Let the precipitate settle (in a dark place) and filter on a tared Gooch crucible and dry on a hot plate. Cool and weigh and calculate the percentage of potassium chloride. Factor 0.519.

Sulfates.—Dissolve five grams of the sample in 100 ml. of distilled water. Filter if necessary. To the filtrate add hydrochloric acid until the solution is slightly acid. Heat the solution to boiling and precipitate the sulfates by adding barium chloride solution slowly and with vigorous stirring. Allow to stand on a hot plate to settle. Filter on a previously ignited and weighed Gooch crucible. Ignite at a red heat to constant weight, cool and weigh as barium sulfate. Calculate the percentage of potassium sulfate by using the factor 0.747.

When the Sulfates are Under 1%.—A two and one-half gram sample is dissolved in about 100 ml. of distilled water and then made slightly acid with hydrochloric acid. Filter if necessary. Transfer the solution to a 250-ml. volumetric measuring flask and dilute to 250 ml. From this solution draw off 25 ml. with a pipette and drain into a previously ignited and weighed platinum dish. Evaporate the solution to dryness and then heat gently (to avoid

[15] By G. E. Fisher, Lefax, 12–561. By courtesy of J. C. Parker, President Lefax, Philadelphia.

spattering of the residue) to low redness or to the point where the chlorides just begin to fuse. Cool and weigh and note as combined chlorides.

The precipitate in the platinum dish should then be taken up with the smallest possible amount of water and to it add seventeen times the weight of the combined chlorides, of a solution of chloroplatinic acid (1 gram platinum to 10 ml.). Evaporate this solution to a thick syrup, and take it up with 25 ml. of 95% alcohol and filter through a tared Gooch crucible and wash with 95% alcohol until the washings are colorless. It is then dried at about 160° C., cooled and weighed. The washings and residues should be preserved for the recovery of the platinum.

$K_2PtCl_6 \times 0.307 = KCl.$

$$KCl - \left\{ \begin{matrix} K_2SO_4 \text{ reduced to chlorides} \\ KCl \text{ as impurity} \end{matrix} \right\} = KCl \text{ as } K_2CO_3.$$

$$\frac{KCl \times 0.926 \times 100}{0.25} = \%\ K_2CO_3.$$

Combined chlorides—KCl = NaCl.

$$\frac{NaCl \times 0.905 \times 100}{0.25} = \%\ Na_2CO_3.$$

When the Sulfates are Over 1%.—To the 25 ml. as obtained above and heated to boiling add barium chloride in slight excess. Let it settle and filter. Then to the filtrate add ammonium carbonate in excess to precipitate the excess of barium. Filter. Evaporate this filtrate to dryness and ignite very carefully to decompose the excess ammonium carbonate and fuse the combined chlorides. Then proceed as outlined above when the sulfates are not in excess of 1%.

The potash residues and washings should be saved and the platinum recovered as follows: The washings and residues are combined and dissolved in hot distilled water. Add sodium formate and sodium hydrate and heat the solution until the platinum is precipitated. Filter and ignite, cool and weigh. Dissolve this residue in aqua regia and evaporate with successive additions of hydrochloric acid until all the nitric is expelled. Then pass chlorine through the solution and evaporate to a syrup to decompose the excess hydrochloric acid. Filter and ignite and weigh and correct for the amount not dissolved. Make up the solution with distilled water so that 10 ml. contains 1 gram of platinum.

Feldspar, Kaolin and China Clay.—These are the chief sources of alumina in glass batches and their frequent examination is to be encouraged. They all contain silica, iron and alumina but in different proportions. Kaolin and China clays are examined for moisture whereas feldspar usually is not. Therefore the same methods of analysis may be carried out for these three materials.

Not more than 0.5 gram sample should be weighed out. (This is done because the alumina precipitate is so voluminous that if larger samples are taken the precipitate is too bulky to handle well and losses may occur.) This is mixed thoroughly with about four grams of sodium potassium carbonate in a

platinum crucible and fused. Digest the fusion in dilute hydrochloric acid and distilled water. Then transfer to a porcelain evaporating dish and evaporate to dryness and bake for about half an hour. Take it up with hot distilled water and dilute hydrochloric acid and filter. Wash the residue with hot water until entirely free from chlorides. Preserve the residue. Make a second dehydration on the filtrate and digest as above, filtering and washing. Combine the residues from the two filtrations and ignite them slowly at first in a clean platinum crucible. When the residue is snow white and to constant weight, cool and weigh. Then moisten the residue with dilute sulfuric acid and make the crucible three quarters full of hydrofluoric acid and evaporate to dryness. (Sometimes it may be necessary to make a second hydrofluoric evaporation.) Ignite, cool and weigh and report the loss in weight as silica. The residue remaining in the crucible may be fused with potassium bisulfate or sodium potassium carbonate and the fusion added to the filtrate remaining from the silica.

To this solution then cautiously add ammonium hydroxide until it is just alkaline and a dense voluminous precipitate comes down. Transfer the beaker to a flame and boil the solution for a few minutes. Allow the precipitate to settle and then filter and wash with hot distilled water. Preserve the filtrate. After the residue is thoroughly washed, place a clean beaker under the funnel and pierce a hole in the paper and wash the residue through with hot water and dilute hydrochloric acid. Be sure to wash the paper thoroughly because any residue remaining and lost will make the results inaccurate. The residue will be dissolved in dilute hydrochloric acid and reprecipitated with ammonium hydroxide, boiled, filtered and washed as described above. The residue is then ignited in a tared platinum crucible, cooled and weighed and reported as (R_2O_3), $Al_2O_3 \cdot Fe_2O_3$. This residue should then be fused with potassium bisulfate or sodium potassium carbonate and the fusion taken up with dilute sulfuric acid. The iron may then be reduced by a choice of methods and titrated with a standard solution of potassium permanganate. The filtrate from the second precipitation of alumina should be combined with the main solution.

The solution is then brought to boiling and, while hot, add about 20 ml. of a saturated ammonium oxalate solution and stir constantly. Then add a few ml. of ammonium hydroxide. Allow the precipitate to settle for several hours and then filter. Wash well with a 2% solution of ammonia water. Ignite the residue at full blast, in a tared platinum crucible, until the weight is constant. Cool and weigh as calcium oxide and report it as such.

Concentrate the filtrate by boiling and while hot add a few ml. of microcosmic salt solution and then ammonium hydroxide. Stir vigorously and constantly. Allow the precipitate to settle for several hours and then filter. Dry the residue and paper before igniting. Then ignite in a tared platinum crucible, cool and weigh as magnesium pyrophosphate. Calculate the percentage of MgO by using the factor 0.362.

If the alkalies in feldspar are desired by other than the difference method, a separate sample may be used and the alkali determined as previously described.

For moisture in kaolins and clays a five gram sample is weighed out and placed in a tared porcelain dish and transferred to a hot plate or oven and heated to about 110° C. for several hours or over night. The loss in weight is reported as moisture.

Barium Carbonate.—Weigh out a one gram sample and dissolve it completely in hydrochloric acid. When dissolved, transfer the solution to a porcelain evaporating dish and evaporate to dryness on a hot plate at 110° C. This residue is then taken up in hot dilute hydrochloric acid and filtered and washed with hot water until free from chlorides. Ignite in a previously ignited and weighed platinum crucible, cool and weigh. This residue is then moistened with dilute sulfuric acid and then the crucible is half filled with hydrofluoric acid and evaporated and ignited, cooled and weighed. The loss in weight is reported as silica. If any residue remains, it is fused with sodium potassium carbonate and added to the main solution.

Separation of Iron and Alumina.—A small amount of ammonium chloride is added to the solution and precipitation of iron and alumina is effected by ammonium hydroxide in the usual way. After ignition and weighing, the residue is fused in sodium potassium carbonate and the iron reduced and titrated with a standard solution of potassium permanganate in the usual way. Reduction of iron may be accomplished in various ways described in the Chapter on Iron, Vol. I.

Separation of Barium from Strontium and Calcium.—Evaporate the filtrate nearly to dryness. Take up with about 300 ml. of distilled water and add 5 or 6 drops of acetic acid with enough ammonium acetate to neutralize any free mineral acid present. Heat the solution and add an excess of ammonium chromate. Allow the barium chromate precipitate to settle for an hour or more, filter on a weighed Gooch crucible and wash with water containing ammonium chromate until free from strontium and calcium. Then wash with distilled water until free from ammonium chromate. Dry the precipitate at 110° C. and ignite gently and finally to a dull red heat. Cool and weigh as barium chromate. Calculate to barium carbonate by using the factor 0.7786.

Separation of Strontium and Calcium.—To the filtrate from the barium solution add about one ml. of nitric acid. Heat the solution and make it alkaline with ammonia followed by ammonium carbonate. Strontium carbonate and calcium carbonate will be precipitated. Dissolve the carbonates in hydrochloric acid and reprecipitate from a hot solution with ammonia and ammonium carbonate. Filter. Wash with hot water. Dissolve the precipitate in the least amount of nitric acid and wash into an evaporating dish. Evaporate to dryness and heat for about an hour at 160° C. Pulverize this mass and mix with a few ml. of ether-alcohol solution. Make several extractions in this way and decant into a flask. The residue is again dried, pulverized and washed into the flask with ether-alcohol solution. Digest with shaking. Wash the residue onto a filter previously moistened with ether-alcohol solution. Strontium nitrate remains, which is dissolved in water. To this water solution add dilute sulfuric acid in slight excess and then an equal volume of alcohol. Allow the precipitate to settle for several hours. Filter on a previously ignited and weighed Gooch crucible and wash several times with a 50% alcohol solution. Dry thoroughly and weigh as strontium sulfate. Compute the sulfate to carbonate by using the factor 0.803.

Determination of Calcium.—Calcium remaining in solution is estimated by making the solution slightly ammoniacal, heating and adding ammonium oxalate with vigorous stirring. Allow the precipitate to settle and then filter and wash with a very dilute ammonia solution. Ignite slowly at first, and

finally at full blast. Cool and weigh as calcium oxide. Compute to calcium carbonate by the factor 1.7847.

Determination of Magnesium.—The magnesium is determined in the filtrate from the calcium. Boil off the ammonia and, while the solution is still hot, add a slight excess of microcosmic salt with constant stirring. Then make the solution alkaline with ammonia and stir. Allow the precipitate to settle over night and filter and wash with a dilute ammonia solution. Dry the residue before igniting. Ignite in a previously ignited and weighed platinum crucible until white. Cool and weigh as magnesium pyrophosphate. Calculate to magnesium carbonate by using the factor 0.75719.

If only the barium content is desired, a short method may be used. After the silica is removed, the filtrate is treated with sulfuric acid, added a drop at a time, and stirred vigorously. The precipitate is allowed to settle and then filtered on a Gooch crucible which has been ignited and weighed. Wash with water containing a few drops of sulfuric acid and finally with hot water. Ignite gently at first and finally at a red heat. Cool and weigh as barium sulfate and compute to barium carbonate by using the factor 0.8455.

Any residue remaining after the hydrofluoric evaporation of silica is calculated as barium sulfate and computed to barium carbonate.

Lime.—Weigh out 0.5 gram sample into a beaker. Cover it with 10 ml. of distilled water and then 10 ml. of hydrochloric acid and heat until clear. Filter and wash several times. Transfer the filter paper to a clean platinum crucible and ignite. Then add about 1 gram of sodium potassium carbonate and fuse. Take up the fusion in dilute hydrochloric acid and add it to the main solution which is then transferred to an evaporating dish and evaporated to dryness. Take up the residue with dilute hydrochloric acid and heat and filter. Wash with hot water until free from chlorides. Preserve the residue and perform a second dehydration as above. Filter and wash and add this residue to that of the first dehydration and ignite in a previously ignited and weighed platinum crucible. Cool and weigh as silica. Correction need not be made on the silica.

To the filtrate from the silica add a small piece of litmus paper and add ammonium hydroxide until it is just alkaline. Heat to boiling and filter. Wash the residue with hot water until free from chlorides. Ignite the residue in a tared platinum crucible. Cool and weigh as (R_2O_3) the combined oxides of iron and alumina. This residue is fused in sodium potassium carbonate or potassium bisulfate, dissolved and the iron reduced and titrated according to the method given in the Chapter on Iron, Vol. I.

The filtrate from the iron and alumina precipitation is heated to boiling and about 20 ml. of a saturated solution of ammonium oxalate is added with vigorous stirring. Allow the precipitate to settle and then filter and wash with hot water. Transfer the precipitate and filter paper to the original beaker and dissolve it in 10 ml. of sulfuric acid and 40 ml. of distilled water. Heat this solution to 70° C. and titrate it with a standard solution of potassium permanganate. Compute the results to calcium oxide.

The filtrate from the calcium is concentrated by boiling. To the hot solution is added a solution of microcosmic salt with constant stirring. It is then made strongly alkaline with ammonium hydroxide. Allow the precipitate to settle for several hours and then filter and wash with a 5% ammonia solution.

Dry the precipitate and paper and, when dry, separate them and ignite separately. If there is considerable residue, it is advisable to ignite in a porcelain crucible. The residues are cooled and weighed, their weights combined and computed to magnesium oxide.

If it is desired to determine the strontium present, refer to the method outlined under the examination of Barium Carbonate.

ANALYSIS OF PRINTING INKS [16]

1. Separation of Oil and Pigment.—Readily effected by mixture of 3 parts ether, 1 part benzene. About 50 g. of ink (avoiding the hard surface film) is placed in a weighed glass tumbler of about 300 ml. capacity, a small amount of solvent added, and the whole stirred thoroughly until a homogeneous mixture is obtained. The glass is then filled with the solvent to about $\frac{1}{2}$ in. of top, and the whole again stirred. It is next placed in the metal cup of the centrifuging machine, and the space between the glass and metal cups filled with water in order to equalize the pressure of the liquid inside the glass. Placing a rubber disk at the bottom of the metal cup has been found to lessen materially the danger of breakage. The metal cup and contents are then counter-balanced, most conveniently by either a second sample of the same ink or another sample of ink, and then both are placed in the machine. For web-press and flat-bed inks 2000 r.p.m. for 10 minutes is sufficient. Where carbon black has been used, it has frequently been necessary to run the machine at 2600 to 2800 r.p.m. for 20 or 30 minutes. The clear liquid is decanted through a pleated filter into a glass bottle, a further quantity of solvent added, and the process repeated. Usually three treatments suffice to give practically complete separation. The glass and contents are dried at about 90° C. and on cooling, reweighed. The increase in weight is the pigment, which is calculated to percentage. The amount of pigment on filter paper should be negligible if centrifuging has been efficient.

2. Analysis of the Oil.—May contain linseed oil, hard gums, rosin, rosin oil, mineral oils, and bituminous substances. The last mentioned, when present, must be judged largely by their color. Sufficient of the solution from the separation of the oil and pigment to leave a residue of about 5 g. is evaporated in a weighed beaker; 50 ml. of normal alcoholic potash is added, the beaker covered with a watch glass, and heated on a steam bath for several hours, stirring frequently to assist saponification. When the latter is complete, the watch glass is removed and the alcohol distilled off. The residue is transferred to a separatory funnel with successive portions of water, using in all about 100 ml., and extracted with petroleum ether until no further oil is obtainable. Four extractions are usually sufficient. The petroleum ether fractions are united in

[16] By J. B. Tuttle and W. H. Smith. Tech. Paper No. 39, U. S. Bur. of Standards.

another funnel, washed with water until the wash water gives no further alkaline reaction, filtered into a weighed beaker, the petroleum ether distilled off, and the residue dried at 95° C., cooled, and weighed. If this unsaponifiable matter is over 2%, it indicates the presence of something else than linseed oil and hard gums. The wash water from the first two washings should be united with the water layer in the first separatory funnel. This unsaponifiable matter is tested for rosin oil by heating a small portion of the oil with 10 ml. of acetic anhydride, allowing it to cool, and adding a drop of H_2SO_4, sp.gr. 1.63. A violet coloration indicates rosin oil.

If the test for rosin is positive, the alkaline water solution which has been extracted with petroleum ether is made acid with HCl (there is usually sufficient dye present from the ink to act as indicator), and the fatty acids which are thus liberated are extracted with successive portions of ethyl ether. These extracts are united, washed free from acid and salts, and evaporated in a small beaker.

A quantitative determination of the rosin may be made as follows: The fatty acids are dissolved in 20 ml. of 95% alcohol, a drop of phenolphthalein is added, and then strong caustic soda (1-NaOH, 2-H_2O) until the reaction is just alkaline. The solution is heated for a few minutes, allowed to cool, and then transferred to a 100-ml. stoppered graduated cylinder. The latter is filled to the 100 ml. mark with ether, 2 g. of powdered silver nitrate crystals is added, and the mixture shaken vigorously for 15 minutes. When the insoluble salts have settled, 50 ml. of clear solution (containing the silver salts of rosin) is pipetted off into a second 100-ml. cylinder, and shaken with 20 ml. dilute HCl (one acid to two water). The ethereal layer is drawn off, and the aqueous layer is shaken twice with ether. The ether extracts are united, washed with water, and the ether distilled off in a weighed beaker. The residue (rosin) is dried at 100° to 115° C., cooled, and weighed. The results are calculated on basis of the original weight of oil.

3. Analysis of the Pigment. (*a*) *Black Inks.*—Ignite, at the lowest possible temperature, a weighed quantity in a porcelain crucible (presence of Pb prohibits Pt), the loss on ignition represents lampblack, the carbon of boneblack (should there be any present), aniline dyes, and undissolved oils or gums. Prussian blue is decomposed by heat, part of it being volatilized, the iron remaining as iron oxide. The residue from the ignition contains any added mineral matter of the pigment, lead or manganese from the driers, iron oxide from the Prussian blue, or iron oxide added as such (the so-called magnetic pigment), calcium phosphate if boneblack is present, and alkali or calcium carbonates from the soaps present. The ash is analyzed quantitatively for insoluble matter, Pb, Fe, Mn and Ca. One quarter gram of the ash is heated to dull redness in a porcelain crucible for a few minutes, cooled in a desiccator, and weighed. This is transferred to a 250-ml. beaker, using conc. HCl to dissolve any material that may stick to the crucible. About 25 ml. of conc. HCl is added, the beaker covered with a watchglass, and after heating until as much as will go in solution is dissolved, the cover is removed and the solution evaporated to dryness. The residue is moistened with a few drops of concentrated HCl, 50 to 75 ml. of boiling water added, and the solution is filtered, washing thoroughly with hot water. The filter paper and residue are ignited and weighed, and the product is called "insoluble matter."

Fifty ml. of 10% H_2SO_4 is added to the filtrate from the previous determi-

nation and evaporated down until the solution fumes strongly. This is cooled, diluted carefully with about 100 to 150 ml. of water, and heated on the steam bath until any basic ferric sulfate which sometimes separates is redissolved. The precipitate containing the lead sulfate is now filtered off. It is dissolved in ammonium citrate or acetate, filtered from any insoluble matter, the filtrate made strongly acid with H_2SO_4 and the precipitated lead sulfate filtered off on a Gooch crucible, ignited, and weighed. The insoluble matter from the ammonium acetate solution should be examined for Ca and Ba.

Another method for the determination of the lead is to neutralize almost all the acid present with sodium carbonate, saturate the solution with hydrogen sulfide, filter off the precipitated lead sulfide, dissolve it in fairly strong nitric acid, and determine the lead as sulfate by the addition of sulfuric acid as above. In this case, solution in ammonium acetate is omitted. The former method is of advantage where qualitative tests show that there is very little manganese present, and it is desired to determine only the iron. The iron is reduced to the ferrous condition by passing the solution through a Jones reductor, and the ferrous sulfate titrated with a standard solution of $KMnO_4$, which has been standardized with sodium oxalate.

Iron is separated from manganese and other metals which may be present by precipitation with ammonia, the precipitate being filtered off, dissolved in HCl, reprecipitated with ammonia, and again filtered. It is now dissolved in HCl, sulfuric acid added, and evaporated down until all the HCl is removed; the solution is diluted and the iron determined as before. Before the addition of the ammonia, if H_2S has been used, the solution should be boiled until it is removed, and nitric acid added to oxidize the iron to the ferric condition. H_2S is now passed into the ammoniacal solution from the iron precipitation. This is allowed to stand over night, and the precipitate, if there is any, is examined for manganese. Should there be much manganese, the sulfide can be filtered off, and the quantitative determination made by conversion into the pyrophosphate.

If it is desired to determine the calcium, this can be done after the filtration from the ammonium sulfide. (If phosphates are present—as, for instance, if boneblack is present—a basic acetate separation is required.) In either case the lead should be separated by H_2S. The filtrate from the manganese sulfide is heated on the steam bath until the H_2S is removed, ammonia and ammonium oxalate are added, and the precipitated Ca oxalate is determined either as oxide or sulfate.

The percentage of ash will be of great assistance in determining the nature of the pigment. Black oxide of iron is only slightly changed on heating, being completely oxidized to ferric oxide. Boneblack is composed largely of calcium phosphate, yielding the greater part of its weight as ash. The presence of any large amount of phosphoric acid will be sufficient evidence that boneblack has been used.

Prussian blue should be tested for qualitatively in the dry pigment. For this purpose 1 g. of pigment is moistened with 2 or 3 ml. of normal alcoholic potash, heated on the steam bath until the alcohol is removed, 5 ml. of water added, and the insoluble matter filtered off. The filtrate is made acid with HCl, and filtered again if necessary. When ferric chloride is added, a blue precipitate will be obtained if Prussian blue is present. If blue dye obscures

the reaction, the solution is again made alkaline and filtered, made acid with HCl as before, and copper sulfate added. The precipitate is filtered and washed thoroughly. In this case we will have reddish-brown copper ferrocyanide. It is advisable, in case of doubt, to add a small amount of Prussian blue to the pigment, and make a check test. In the absence of black oxide of iron we may assume that all of the iron in the filtrate is due to the Prussian blue. The percentage of Fe_2O_3 in the ash, multiplied by the percentage of ash in the pigment, multiplied by the factor 1.53, will give, roughly, the amount of Prussian blue present. The factor 1.53 is obtained by the ratio $Fe_7(CN)_{18}$ to Fe_2O_3. An approximate determination of the dyes can be made by extracting with alcohol. When the presence of oxide iron is suspected, 1 g. of pigment is wrapped in filter paper and the dye extracted with alcohol. When all of the dye has been extracted, the paper and contents are dried and the nitrogen is determined in the residue by the Kjeldahl method. From the nitrogen thus determined the Prussian blue is calculated, using the factor 3.41. The Fe_2O_3 present in this amount of Prussian blue is deducted from the total Fe_2O_3 found in the ash. The remainder will be the percentage of iron from the magnetic oxide. The formula of the latter is theoretically Fe_3O_4, and proper calculation should be made.

(*b*) *Blue Inks.*—A weighed quantity of pigment is ignited as under black pigments. The ash is analyzed same as before, determining only lead, manganese, and iron if the qualitative tests show that Prussian blue is present. The lead and manganese are reported as metallic driers, the iron is calculated to Prussian blue, and the remainder reported as mineral filler. The presence of ultramarine will be shown by the blue color of the ash. In this case the ash is reported after deducting the Pb+Mn. Dyes are determined by alcohol extraction.

(*c*) *Red Inks.*—Vermillion (mercuric sulfide) is readily detected by taking a small quantity of pigment, covering it with 4 or 5 ml. aqua regia, and heating gently. This is diluted with five volumes of water, filtered, and stannous chloride added to the filtrate; a grayish precipitate of mercury will be formed if even a very small amount is present.

Quantitative method: Dissolve the mercuric sulfide in aqua regia, and after nearly neutralizing the diluted solution to precipitate the mercuric sulfide with H_2S, weigh the precipitate on a Gooch crucible, observing all the precautions to eliminate sulfur which separates during the precipitation.

The following procedure has also been found of value: One g. of the pigment is treated with a slight excess of ammonium sulfide. Sodium hydroxide is then added, while stirring. The beaker is placed upon the steam bath, adding more alkali if necessary, until all the mercuric sulfide has passed into solution. An excess of alkali should be avoided. The solution is allowed to cool, filtered, and the residue washed thoroughly. To the filtrate sufficient ammonium nitrate to reprecipitate the mercuric sulfide is added, and it is then boiled to expel ammonia. The precipitate is allowed to settle, and the supernatant liquid decanted through a weighed Gooch crucible. The residual mercuric sulfide is boiled with a little sodium sulfide solution to remove free sulfur, and is then transferred to the crucible where it is washed with hot water, until it no longer reacts with silver nitrate solution. It is dried at 110° and weighed. The

pigment is ignited, and the ash analyzed for lead and manganese. The rest of the ash is reported as mineral filler.

(*d*) *Green Inks.*—The coloring matter may be chrome green, green lake, or dye. Some of the darker shades are obtained by the addition of lampblack. The ash of the pigment is determined as usual. Part of this ash is taken and tested qualitatively for chromium. If present, the ash should be tested for the following substances: $PbCrO_4$, $PbSO_4$, PbO, $BaSO_4$, $CaSO_4$, Fe_2O_3, and Mn_3O_4. For the determination of sulfur, 0.250 g. of the ash and 5 g. of a mixture of equal parts of potassium nitrate and sodium carbonate are fused in a porcelain crucible over a sulfur-free flame. The cooled mass is extracted with hot water and filtered. The filtrate is acidified with HCl, heated to boiling, and 10 ml. 10% barium chloride added. After standing over night, the precipitated barium sulfate is filtered off, ignited, and weighed. The solution should be sufficiently acid to prevent any significant contamination of the barium sulfate with barium chromate.

For the determination of barium, the insoluble matter is dissolved in HCl, the solution made nearly neutral with sodium carbonate, and H_2S is passed into the solution until all the lead is precipitated. The lead sulfide is filtered off, the filtrate heated to boiling, and 10 ml. of 10% H_2SO_4 added. The barium sulfate is treated as directed under the determination of sulfur.

A fresh portion of ash is mixed with sodium peroxide and fused in a nickel crucible. The cooled melt is dissolved in hot water and filtered. Carbon dioxide is passed into the filtrate, and the latter heated again on the steam bath in order to precipitate any lead which may be held up by the caustic alkali. Any insoluble matter which may separate is filtered off. The filtrate is made strongly acid with HCl, KI added, and the liberated iodine titrated with a standard $Na_2S_2O_3$ solution. From the amount of thiosulfate used the amount of CrO_3 present is calculated.

The two precipitates from the previous determination are combined and used for the determination of Pb, Fe, Mn, and Ca. They are dissolved off the filter paper with HCl, the solution is nearly neutralized with sodium carbonate, and H_2S passed into the solution. The precipitated lead sulfide is filtered off, dissolved in nitric acid, and determined as sulfate, as directed under black pigments.

The filtrate from the lead sulfide is heated until all the H_2S is boiled off. If any sulfur separates, it is filtered off. Two or three ml. of nitric acid is added and the solution again heated. It is then made alkaline with ammonia and filtered. The precipitate is dissolved in HCl and reprecipitated with ammonia, the precipitate again filtered off and the filtrate united with that from the first precipitation. This solution is reserved for the determination of manganese. The second precipitate of iron is dissolved in HCl, converted into the sulfate, and the iron determined as under black pigments.

The united filtrates from the iron precipitation are saturated with H_2S, allowed to stand over night, and then filtered. If there be a sufficient amount of manganese present, it can be determined quantitatively as pyrophosphate; otherwise qualitative identification will be sufficient.

It is safe to assume that all chromium was present originally as lead chromate, and it should be so calculated. The iron oxide should be calculated to Prussian blue, provided there is a positive qualitative test. Any barium present

should be calculated to sulfate; if there is any question as to its being originally present as carbonate, the ash of the pigment is treated with very dilute HCl, the solution filtered and the filtrate tested for barium. Barytes is difficultly soluble in cold dilute HCl. In the absence of barytes the sulfur present is calculated to lead sulfate. The excess of lead over that required for the lead chromate and sulfate may be considered as drier. China clay may be present either as an added part of the chrome green, or as the base of a green lake. In such cases, the undetermined portion of the ash should be reported as mineral filler. Green dyes are determined by extraction as usual. In the absence of chrome green the pigment is ashed, and the ash analyzed for lead and manganese only, the balance being reported as mineral fillers. If lampblack has been used to produce a dark shade of green, it can be tested qualitatively by taking a small portion of the pigment, treating it with strong alkali, and filtering through a Gooch crucible, washing first with hot water, and finally with moderately concentrated HCl. Lampblack will show a black residue, which will disappear on ignition. It is generally classed with the volatile constituents, which are then reported as aniline dye, lampblack, undissolved oil, etc.

The analytical methods included the essential constituents of inks: the determination of iron, tannic acid, gallic acid, total solids, ash, acidity, etc. The specific gravity of the ink will indicate the amount of dissolved material present. F. F. Rupert, in a paper on the examination of writing inks (J. Ind. Eng. Chem., **15**, 489, 1923), emphasizes the importance of the physical tests of color, permanence, stability and noncorrosiveness. The following tests are suggested.

Streak Tests.—A sheet of a good quality of bond paper placed on a pane of glass and held by clamps serves for taking the streak. The streak is made by a pipette 25 cm. long, 3.5 mm. in diameter with a file mark 62 mm. from the tip. Ink filled to the mark (0.6 ml.) is tested by drawing the pipette over the surface of the paper, at the same time allowing the ink to flow.

Penetration and Fluidity.—The ink should penetrate into the fibres of the paper but should not pass through. A normal ink will give an oval head (where the streak begins) and the width of the line will be uniform. A poor ink gives a wide head and the streak narrows rapidly. Stickiness should be observed.

Temporary Color.—The mark should be dark enough to be easily seen. A speckled appearance indicates that the ink contains a dye which is not in solution.

Permanent Color.—The streak is exposed to diffused light for 7 days in an atmosphere free from chemical fumes and dust. A comparison is made with a standard ink. The paper is now cut into crosswise strips 1 inch in diameter. The top and bottom strips are set aside as blanks.

Exposure to Light.—Strips containing the streaks are exposed to sunlight or ultra violet rays for a period 48 hours to two weeks or longer and the ink thus exposed compared with the blanks.

Exposure to Weather.—The exposed sample is inspected weekly.

Exposure to Water and Reagents.—Tests in water, in dilute ammonia (1 : 10), HCl 2% solution, bleaching powder or sodium hypochlorite of 0.005 N available Cl.

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Pacific Salmon Investigations
U. S. Fish & Wildlife Service
Seattle, Washington.

Stability.—Note sediment in original. Filter two portions, one into a bottle which is later stoppered, the other portion into an open bottle covered by a piece of paper. Filter each after a period of a week or more and note sediment on filter paper.

Corrosion.—The effect of the ink on steel pens, immersed in the ink for a period of time, at least one week. The pens are weighed before and after the test.

Comparison and Rating.—The system is subordinated to the knowledge of the purpose for which the ink is to be used. For further details the reader is directed to the article by Rupert.

DETERMINATION OF PEROXIDES [17]

DETERMINATION OF HYDROGEN PEROXIDE. KINGZETT'S IODIDE METHOD [18]

The method depends upon the reaction—

$$H_2O_2+2KI+H_2SO_4=I_2+K_2SO_4+2H_2O.$$

Procedure.—Approximately 2 grams of potassium iodide are dissolved in 200 ml. of water, conveniently in an Erlenmeyer flask, and 30 ml. of dilute sulfuric acid (1 : 2) are added. Three good drops of N Ammonium Molybdate are added to catalyze the reaction. Ten ml. of hydrogen peroxide solution (the sample having been diluted to contain approximately 0.6% by weight of H_2O_2) are run in from a burette, agitating the mixture during the addition. After standing five minutes, the liberated iodine is titrated with N/10 thiosulfate.

$$1 \text{ ml. N/10 } Na_2S_2O_3=0.001701 \text{ gram } H_2O_2.$$

DETERMINATION OF HYDROGEN PEROXIDE BY THE ARSENIOUS ACID METHOD OF JAMIESON [19]

The method is based on the reactions—

$$As_2O_3+2H_2O_2=As_2O_5+2H_2O$$

and

$$As_2O_3+KIO_3+2HCl=As_2O_5+ICl+KCl+H_2O.$$

Procedure.—A measured quantity of N/5 solution of As_2O_3, which must be in excess of that required by the peroxide taken for analysis, is placed in a 500 ml. glass stoppered bottle, and 10 ml. of 10% NaOH added, followed by a

[17] Selections by W. W. Scott.
[18] J. Chem. Soc., 1880, 792.
[19] Am. Jour. Sci., **44**, 150–2 (1917).

measured volume of the peroxide from a burette (15–20 ml. of the solution made by diluting 50 ml. of the commercial peroxide to 500 ml.) with gentle agitation of the contents of the bottle. After standing two minutes, 40 ml. of concentrated HCl are added and the stopper inserted in the bottle. The contents of the bottle are shaken violently, holding the stopper in place. The stopper is now cautiously released and the confined gas allowed to escape. Six to seven ml. of chloroform are added and the unoxidized As_2O_3 is titrated with N/5 KIO_3 solution, shaking the closed bottle after each addition, until the iodine color in the chloroform has disappeared.

The ml. As_2O_3 solution used minus the ml. equivalent of KIO_3 gives the ml. of arsenous acid required by the hydrogen peroxide.

$$1 \text{ ml. N/5 } As_2O_3 = 0.0034016 \text{ gram } H_2O_2.$$

This method is not influenced by the presence of organic preservatives as is the permanganate method which follows.

PERMANGANATE METHOD FOR DETERMINATION OF HYDROGEN PEROXIDE

The procedure depends upon the reaction—

$$5H_2O_2 + 2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

Procedure.—Fifty ml. of the commercial peroxide are diluted to 500 ml. 10 ml. of this diluted solution are taken for the test. This sample is further diluted to 400 ml. in a beaker, 10 ml. of dilute sulfuric acid (1 : 4) are added and the mixture titrated with N/10 $KMnO_4$ reagent to a pink coloration.

Should the first drop or two of permanganate cause a pink color it indicates that an insufficient quantity of sulfuric acid is present and an additional amount should be added.

$$1 \text{ ml. N/10 } KMnO_4 = 0.001701 \text{ gram } H_2O_2.$$

Notes.—If it is required to report the number of volumes of oxygen liberated by one volume of the peroxide "per cent per volume," multiply the per cent weight of H_2O_2 by 112 and divide the result by 34.

Since H_2O_2 decomposed to H_2O+O, one gram molecule of peroxide sets free one gram atom of oxygen, equivalent to 11,200 ml. Therefore 100 grams commercial $H_2O_2 = \%H_2O_2 \times 11{,}200$ divided by 34, and 1 gram = 1/100 of this.

COMPLETE ANALYSIS OF SODIUM SULFIDE [20]

Sodium Sulfide.—Commercial sodium sulfide is marketed in three forms: Fused solid, flaked solid, and crystals. For manufacturing, control analyses may also be called for on various liquors. The same general methods can be used in these cases by suitably adjusting the sample and aliquot sizes.

[20] By courtesy of The Dow Chemical Co., Midland, Michigan.

NOTE 1.—The following handling of sample may be used conveniently in many cases, particularly with moist material: Weigh a large sample, say 50 or 100 grams accurately, dissolve, and make to 500 or 1000 ml. volume. The "water insoluble" should be run on separately weighed samples as indicated, the filtrate being discarded. The water insoluble material should be allowed to settle, on the large made up sample, and an aliquot giving 10–12 g. made to 500 ml. for the sulfides, sulfite, etc., proceeding as outlined. Suitable aliquots taken from the strong made-up solution can then be taken for the Na_2CO_3 and NaCl determinations.

Water Insoluble.—Weigh accurately 10 to 12 grams of the 60% sulfide, or estimate an equivalent amount of other sulfide materials; transfer to a stoppered flask and dissolve in approximately 150 ml. of water and stand for several hours or overnight in a warm place, as on a radiator or top of an oven. If necessary to proceed without much delay, warm to about 70° C., stand an hour, and filter through a 30-ml. tared Gooch crucible. A fairly thick pad must be used. The filtrate obtained should be clear. Wash with water, and dry at 100° C. Weigh the insoluble residue.

$$\frac{\text{Grams gain} \times 100}{\text{Sample weight}} = \%\ H_2O \text{ Insoluble.}$$

Make the filtrate to 500 ml. volume for the analysis.

FeS.—This is included with the water insoluble material, Fe being present as FeS. When Fe is called for, the following method may be used:

Weigh about 10 grams, dissolve in 100 ml. of water, add 50 ml. concentrated HCl and boil off H_2S. Add a few ml. of HNO_3 and then bromine-potassium bromide solution to clear from sulfur and to oxidize the iron. Boil off bromine, make alkaline with NH_4OH, filter, wash and ignite.

$$\frac{\text{Grams } Fe_2O_3 \times 110}{\text{Grams sample}} = \%\ \text{FeS.}$$

In case Al_2O_3 is present, the precipitate (R_2O_3) should be fused with $KHSO_4$, dissolved, reduced, and titrated with $KMnO_4$.

Ordinarily these determinations are not called for unless the water insoluble runs extremely high.

Use 25.00 ml. aliquots of the 500 ml. solution for all the subsequent determinations, unless other aliquots or separately weighed samples are called for.

A. Total I_2 Titration.—Add a known excess (100 ml.) of N/10 I_2 to a 250-ml. beaker, acidify with 15 ml. N/1 HCl, then pipette in an aliquot of the sample slowly, while stirring. Titrate back with N/10 $Na_2S_2O_3$ solution, using one ml. of starch solution at the end after the iodine color is visibly faded. Add a few drops of methyl red indicator to make sure the solution is acid at the finish. If not, double the amount of N/1 HCl called for, and repeat. I_2 minus $Na_2S_2O_3 = A$. This is Na_2S plus NaHS plus $Na_2S_2O_3$ plus Na_2SO_3.

NOTE 2.—Methyl red indicator used here is made by heating a small amount of the dye with water almost to a boil. From one to five ml. of the cool settled solution may be used.

NOTE 3.—Starch solution used here is made by mixing 5 g. soluble starch with 10 ml. of water, adding 20–30 ml. N/1 NaOH to clear, titrating to phenolphthalein neutral point with N/1 HCl, and diluting to 500 ml.

B. Sulfides.—Place 10 to 12 ml. of ammoniacal zinc chloride reagent into 250-ml. beakers and pipette in aliquots. Mix by swirling and add enough water to thin out the precipitate. Filter off the ZnS and wash well with warm water. Place a known excess of N/10 I_2 (100 ml.) into the original beakers. Acidify the iodine solution with a few ml. of 1 : 1 HCl, and transfer the precipitate to the beaker over the edge of the funnel. This can be done very completely, and without difficulty. Then puncture the tip of the paper, and wash the paper for small amounts of adhering precipitate with warm dilute HCl. The paper should be left on the funnel and the acid wash collected in the original beaker. This should be kept well stirred and small additions of HCl made till the reaction is complete. Titrate the excess I_2 with $Na_2S_2O_3$ as above. Net $I_2 = B$.

This is Na_2S plus NaHS.

Save the filtrates and washings from the ZnS ppt. for *C* and *D*. Any turbidity noted, especially on the top is not due to sulfur or zinc sulfide, but to zinc hydrate. At this point no harm is done by this occurrence. The N/1 ammoniacal zinc chloride will be hydrolyzed on diluting sufficiently.

Note 4.—Ammoniacal zinc chloride reagent. Dissolve 41 g. of c.p. zinc oxide in HCl. The HCl should be in just enough excess to readily dissolve the oxide while being added slowly with stirring. Then add NH_4OH slowly to make approximately neutral, add 200 ml. of water, 150 ml. of concentrated. NH_4OH, and 65 g. of NH_4Cl. Make to one liter. This is roughly a normal solution. Use to precipitate sulfides by adding a slight excess, testing the filtrate with more reagent to be certain that precipitation is complete; with an iodine titration of 80 to 95 ml., 10 ml. of the reagent would be sufficient. It should not be diluted before use, as $Zn(OH)_2$ will precipitate. During an analytical operation this precipitate should not be confused with ZnS. The hydrate will appear during the neutralization, especially if much of the reagent was not used up as a precipitant.

Cadmium chloride reagent may be used by those who are more familiar with its use.

C and D. Thiosulfate and Sulfite.—Make the above mentioned filtrates neutral to methyl red using first N/1 HCl and then N/10 near the end. Disregard the formation of $Zn(OH)_2$, continuing the titration to the pink end-point. Then add 1 ml. of starch indicator and titrate one of the two filtrates with N/10 I_2. Call the ml. used *C*. This equals $Na_2C_2O_3$ plus Na_2SO_3. To the other filtrate add 5 ml. of 10% $BaCl_2$ and filter onto a wet asbestos pad on a Gooch crucible; wash with water, and transfer pad and precipitate back to the original beaker. Add an excess of N/10 I_2, acidify with a few ml. of N/1 HCl, and stir well. Titrate back with N/10 $Na_2S_2O_3$. Ml. N/10 I_2 minus N/10 $Na_2S_2O_3 = D$. This is Na_2SO_3. The formation of a precipitate at this point is a test for sulfite.

E. Alkalinity, Polysulfide Sulfur, and Na_2SO_4.—Titrate aliquots with N/10 HCl, shaking or stirring well throughout the titration, and adding a drop of methyl orange indicator from time to time. The indicator has a tendency to fade, the tendency being overcome as the end-point is approached. Record the ml. to give the pink end-point as uncorrected *E*. The applied correction for carbonate and sulfite will be given under " Calculations," to follow.

Now add two to five ml. of the acid from the burette, in excess of the neutral point. If the solution remains perfectly clear, after several minutes standing, no polysulfide is present. If a cloudiness appears, warm to approximately 70° C. and hold thus for an hour; filter through tared 10-ml. Gooches, being careful to transfer all adhering precipitate. Dry at 80° C. for two hours and weigh back.

$$\frac{\text{Grams} \times 100}{\text{Sample weight}} = \%\ \text{Polysulfide sulfur.}$$

Add 5 ml. of 1–1 HCl to the filtrate and washings from Polysulfide sulfur and boil for three minutes. Add 10 ml. of 10% $BaCl_2 \cdot 2H_2O$. Let stand an hour. Filter through No. 42 Whatman filter paper, or one of equal quality, wash well, ignite, and weigh $BaSO_4$.

$$\frac{\text{g. } BaSO_4 \times .6086 \times 100}{\text{g. Sample}} \times \%\ Na_2SO_4.$$

Na_2CO_3.—Acid sulfide is too weakly acid to decompose carbonates. Sodium carbonate may be present in greater or lesser amounts. The amount of sample to take depends on the amount known to be present or expected. For 2 to 8%, 5 gram samples accurately weighed are suitable. Dissolve a pair in 75 ml. of CO_2-free water, add 25 ml. of 25% ammoniacal ammonium acetate solution. (This solution has enough concentrated NH_4OH added to just turn pink with phenolphthalein indicator added.) After mixing, add 20 ml. of 10% $BaCl_2$ solution, stopper well, mix, and stand overnight. In the morning, filter through asbestos, using a 25- or 35-ml. Gooch crucible. Wash well and transfer precipitate and pad to a 500-ml. assay flask. The pad can readily be loosened with a knife point. Add 100 ml. of water and 100 ml. of N/10 HCl; also several ml. of methyl red indicator. Boil for fifteen minutes. With high carbonate, more acid may be necessary; this will be indicated by changing of the indicator to the alkaline yellow color. Cool and titrate back with N/10 NaOH. (Mls. N/10 HCl − mls. N/10 NaOH = "*T*.") In addition to the back titration, a further correction on the acid must be made for sulfite. Adjust the titrations to the same size sample as follows:

$$\frac{\text{g. Sample for } Na_2CO_3}{\text{g. Sample for } Na_2SO_3} \times D = \text{ml.},$$

Correction for Na_2SO_3: Call D'.

$$\frac{\text{N/10 HCl} - (\text{N/10 NaOH} + D') \times .0053 \times 100}{\text{g. Sample}} = \%\ Na_2CO_3.$$

In many cases too much time will be lost by giving the overnight standing as specified. For control purposes, the time may be shortened to as small a period as ½ hour, introducing a plus error usually under 10% of the Na_2CO_3 present. A somewhat longer standing period, say 4 hours, gives the BaS which forms to some extent, a better chance to decompose.

Calculations:

Thiosulfate—

$$\frac{(C - D) \times .0158 \times 100}{\text{Grams sample}} = \%\ Na_2S_2O_3.$$

Sulfite—

$$\frac{D \times .0063 \times 100}{\text{Grams sample}} = \%\ Na_2SO_3.$$

Sulfide and Acid Sulfide—

Correct *E* for carbonate and sulfite by subtracting the sum of the titrations adjusted for sample size.

$$\frac{\text{g. Sample for } B}{\text{g. Sample for } Na_2CO_3} \times T = (Na_2CO_3 + Na_2SO_3) \text{ mls. on } B \text{ basis—Call } T'.$$

$$E - T' = \text{ml. corrected } E, \text{ or } E'.$$

$$\frac{E' - (B - E') \times .0039 \times 100}{\text{g. Sample}} = \%\ Na_2S, \text{ where } E' \text{ is less than } B.$$

Then

$$\frac{(B - E') \times .0056 \times 100}{\text{g. Sample}} = \%\ NaHS.$$

When E' is greater than B, the mixture is caustic and normal sulfide, then

$$\frac{(E' - B) \times .0040 \times 100}{\text{g. Sample}} = \%\ NaOH$$

and

$$\frac{B \times .0039 \times 100}{\text{g. Sample}} = \%\ Na_2S.$$

Where E' is less than B,

$$\frac{B \times .0039 \times 100}{\text{g. Sample}} = \%\ Na_2S + NaHS, \text{ calculated as } Na_2S.$$

The following equations and example will clarify the above calculations:

(1) $Na_2S + I_2 \rightarrow 2NaI + S.$

(2) $NaHS + I_2 \rightarrow NaI + HI + S.$

(3) $NaHS + HCl \rightarrow NaCl + H_2S.$

(4) $Na_2S + 2HCl \rightarrow 2NaCl + H_2S,$

with I_2—(1) $H \equiv Na_2S = 2$, 1 ml. N/10 $I_2 = .0039$ g. Na_2S.
(2) $H \equiv NaHS = 2$, 1 ml. N/10 $I_2 = .0028$ g. NaHS.

with HCl—(3) $H \equiv NaHS = 1$, 1 ml. N/10 HCl = .0056 g. NaHS.
(4) $H \equiv Na_2S = 2$, 1 ml. N/10 HCl = .0039 g. Na_2S.

Illustration—

	Na_2S	+	$NaHS$	
B	.0039			$-N/10\ I_2 = 80.0$ ml.
		.0028	.0028	
E'				$-N/10$ HCl = 62.0 ml.
	.0039	.0056		
	Na_2S	+	$NaHS$	

E' is less than B—Sample = .5000 g. $\therefore$

Computing by above methods—

$$Na_2S + NaHS = 62.4\%$$
$$Na_2S = 34.3\%$$
$$NaHS = 20.2\%$$
$$20.2 \times 39/28 = 28.1 = NaHS \text{ calc. as } Na_2S.$$
$$28.1 + 34.3 = 62.4 \quad Na_2S + NaHS.$$
$$\frac{80.0 \times .0039 \times 100}{.5000} = 62.4.$$

It will be noted that the "total iodine titration," or reducing value, called A titration has not been used in these calculations, and that this was not called for in duplicate. This titration gives a check on the work. A should always be numerically greater than B. $A - B = C$. After titrating C, or $Na_2S_2O_3$ plus Na_2SO_3, an indirect valuation of Na_2SO_3 may be made. Remove the blue color with a drop of N/10 $Na_2S_2O_3$ and titrate with N/10 NaOH recording the ml.

$$\frac{A - B - (C - 2/3 \text{ ml. N/10 NaOH}) \times .0063 \times 100}{\text{g. Sample}} = \%\ Na_2SO_3.$$

NaCl—

Weigh accurately samples of 2 to 4 grams and dissolve in 400 ml. of water. Add 1 : 1 nitric acid till approximately 10 ml. in excess of the neutral point have been added. Boil gently till the odor of H_2S and SO_2 has disappeared. Cool. Filter off coagulated sulfur. Add a crystal or two of c.p. chromic acid to the filtrate and bring to a boil. Precipitate chloride by addition of a slight excess of 2% silver nitrate solution. With low chloride a few hours standing will give a better formed precipitate. Filter the precipitate on tared Gooch crucibles, 20 or 25 ml. size, and wash free from soluble salts. Dry at 120 to 140° C. for two hours. Weigh back AgCl.

$$\frac{\text{g. AgCl} \times .408 \times 100}{\text{g. Sample}} = \%\ NaCl.$$

Sodium acid sulfide (sulfhydrate) liquor is used in several commercial reactions. The methods and calculations will apply except in the case of free hydrogen sulfide. Using the same letters for designating various titrations, a sample calculation is as follows:

13.9291 grams to 500 ml. volume and 25 ml. aliquots used for sulfides, etc. (.696 g.).

8.174 grams, direct for Na_2CO_3.
$B = 57.50$ ml. N/10 I_2.
$C = .38$ ml. N/10 I_2.
$E = 29.87$ ml. N/10 HCl.
$Na_2CO_3 = 33.05$ ml. N/10 HCl.

$$\frac{.696}{8.174} \times 33.05 = 2.81 \text{ ml. carbonate correction.}$$

E corrected for carbonate = 27.06 ml.

$$\frac{27.06 \times .0056 \times 100}{.696} = 21.7\%\ NaHS.$$

Sulfide as % H_2S—

$$\frac{57.50 \times .0017 \times 100}{.696} = 14.05\%\ H_2S.$$

Factor NaHS to H_2S 34.08/56.07 = .607.
Above NaHS (21.7%) equiv. to 13.16% H_2S.
14.05–13.16 = .89% net H_2S.

Thiosulfate—

$$\frac{.38 \times .0158 \times 100}{.696} = .86\%\ Na_2S_2O_3.$$

Carbonate—

$$\frac{33.05 \times .0053 \times 100}{8.174} = 2.15\%\ Na_2CO_3.$$

Summary—

% H_2S	.89
% HaHS	21.7
% Na_2CO_3	2.15
% $Na_2S_2O_3$	.86

NOTE 5.—Credit for above methods must be given to Sutton's Volumetric Analysis, DuPont Publication, in J. Ind. Eng. Chem., **17**, 176 (1925). Grasselli Chemical Co., 12–18–29, and various Dow Chemical Company chemists.

We are indebted to A. W. Beshgetoor, Chief Analytical Chemist, the Dow Chemical Company, for the section on the complete analysis of sodium sulfide.

PART II

SPECIAL
TECHNIQUES APPLICABLE
TO
DIVERSE SUBSTANCES

ACIDIMETRY AND ALKALIMETRY[1]

The volumetric determination of a free acid or a free base may be accomplished with rapidity and accuracy by neutralization with a known quantity of standard base or alkali as the case may require. The point of neutralization or "end-point" is accertained by means of certain compounds called indicators, which have a different color in acid solutions than in alkaline solutions, the point of transition from one color to the other occurs at the point of neutralization. This end-point may also be recognized by the electrometric method by measuring the change of potential that occurs with the change of concentration of the hydrogen ions in the solution. This potential change is usually large and abrupt at the end-point.

Indicators.—The accuracy of acidimetric and alkalimetric titrations depends, to a considerable extent, on the choice of the indicator used. Indicators are usually dyestuffs, which have one color in an acid solution and another in alkaline solutions. The color change should occur as near as possible to the equilibrium point reached in neutralization. The color change of certain indicators may be due to a difference in color of the dissociated from the undissociated compound or to the presence of certain groups of radicals within the molecule of the compound, called chromophores, which show one color in acid solutions and, by internal rearrangement, another color in basic solutions. This color change depends upon the hydrogen ion concentration of the solution rather than the absolute amount of acid present. The pH range of color change differs with different indicators as is shown in the table given on the following page. It is generally the case that indicators whose color change occurs with a hydrogen ion concentration greater than pH 7 are sensitive to weak bases, while those whose color change occurs with hydrogen ion concentration less than pH 7 are sensative to weak acids. Thus methyl red with color changes between pH 4.2 and 6.3, is sensitive to weak bases, while phenolphthalein with a range of pH 8.2 to 10 is sensitive to weak acids.

Indicators may show a color change at entirely different stages of the chemical reaction, phenolphthalein, for example, in the titration of sodium carbonate, Na_2CO_3 indicates an acid reaction as soon as one of the Na atoms is neutralized and a drop of excess of the titrating acid liberated CO_2. Methyl orange at this stage shows alkalinity, $NaHCO_3$ being alkaline to methyl orange and neutral to phenolphthalein The same difference is shown in the titration of other polybasic compounds.

Among the indicators commonly employed in acidimetry and alkalimetry the list given by Kolthoff and Furman [2] is of special interest; tropeolin 00, pH 1.3 red–3.2 yellow; thymol blue, pH 1.2 red–2.8 yellow; methyl yellow, transition 2.9–4.0, red to yellow; methyl orange, transition interval 3.0–4.4, red to orange; brom phenol blue, pH 3.0–4.6, yellow to violet blue; congo red, 3.0–5.2, blue to red; methyl red, 4.4–6.2, red to yellow; brom cresol green, 4.0–

[1] By Wilfred W. Scott.
[2] "Vol. Anal.," J. Wiley and Sons.

5.6, yellow to blue; chlorphenol red, 5.0–6.6, yellow to red; brom cresol purple, 5.2–6.8, yellow to purple; sodium alizarin sulfonate, 5.5–6.8, yellow to lilac; brom thymol blue, 6.0–7.6, yellow to blue; azolitmin (litmus), 5.0–8.0, red to blue; phenol red, 6.8–8.0, yellow to red; neutral red, 6.8–8.0, red to yellow orange; rosalic acid, 6.9–8.0, yellow to red; cresol red, 7.2–8.8, yellow to red; a naphthol phthalein, 7.3–8.7, yellowish rose to green; curcumin, 7.4–8.6, yellow to red-brown; phenol phthalein, 8.2–10, colorless to red; thymol blue, 8.0–9.6, yellow to blue; a naphthol benzein, 9.0–11.0, colorless to blue; thymol phthalein, 9.3–10.5, colorless to blue; alizarine yellow, 10.1–12.1, yellow to lilac; tropeolin 0, 11.0–13.0, yellow to orange brown; nitramine, 10.8–13.0, colorless to red brown. Certain mixed indicators give a color change more sharply, for example a mixture of brom cresol purple and brom thymol blue, mixed in equal parts. The indicator is greenish yellow at pH 6.0 and blue at pH 6.8. A comprehensive table of mixed indicators is given in Kolthoff and Furman's work.

A list of the more common of the indicators is tabulated below. The pH transition interval, and the color changes are given.

Solutions of Indicators: Brom Cresol Purple.—0.04% alcoholic solution. Changes color at about pH 6.

Methyl Orange.—0.1 g. per 100 ml. of water. Transition interval pH 3.–4.4. Apparent pH of end-point, or pT = 4.

Methyl Red.—The acid is dissolved in alcohol (0.1 g. per 60 ml.) and made up to 100 ml. with water. If the sodium salt is available, 0.1 g. is dissolved in 100 ml. of water. pT = 5.

Methyl Yellow.—0.1 g. in 100 ml. of 90% alcohol. pT = 4.

Phenolphthalein.—1 g. per 100 ml. of 95% alcohol. If 1 or 2 drops of this solution is used per 100 ml. of solution titrated, the end-point is at pH 9. If about ten times as much of the indicator is added per 100 ml. of solution the change appears at pH 8. Cresol red (0.1 g. per 100 ml. 20% alcohol) changes color at pH 8.

Thymol Blue (Thymol sulfone phthalein).—0.1 g. in 20 ml. of hot alcohol; dilute to 100 ml. with alcohol. The indicator has two ranges: Changes from red to yellow at pH 1.2–2.8, pT = 2.6; changes from yellow to blue, pH 8.–9.6, pT = 9.

Mixed Indicators.—1.25 g. methyl red, 0.825 g. methylene blue dissolved in 1 liter of 90% alcohol; 0.75 g. methyl red, 0.025 g. guinea green dissolved in 1 liter of 90% alcohol; 5 g. sodium alizarin sulfonate, 0.625 g. guinea green in 1 liter of water; 5 g. sodium alizarin sulfonate, 1.25 g. indigo carmin in 1 liter of water (A. H. Johnson and Jessie R. Green, Ind. Eng. Chem., Anal. Ed., **2**, 2 (1930)).

ULTIMATE STANDARDS

Constant-boiling hydrochloric acid is generally used as the ultimate standard acid. Benzoic acid and other acids or acid salts, e.g. potassium acid phthalate, are also used.

Sodium carbonate is the best of the alkali standards. This salt may be prepared in exceedingly pure form. It is generally used as the basic material for the volumetric standardization of the acid.

PREPARATION OF PURE SODIUM CARBONATE

Bicarbonate of Soda made by the Ammonia-Soda process may be obtained in exceedingly pure form. The impurities that may be present are silica, ammonia, lime, arsenic, sodium chloride and sodium sulfate. With the exception of silica and lime the impurities may be readily removed by recrystallizing the bicarbonate, decanting off the supernatant solution containing the impurities. The bicarbonate is dried between large filter papers in the hot air oven (100° C.).

Standard Sodium Carbonate is made from this pure sodium bicarbonate by heating at 290° C. to 300° C. in an electric oven. If a constant-temperature oven is not available a simple oven may be improvised by use of a sand bath and a large beaker or a sheet-iron cylinder covered at the upper end as shown in Fig. 299. A thermometer passing through this shield registers the temperature of the material, within a large platinum crucible. This crucible rests upon a triangle, so that the bicarbonate is entirely surrounded by an atmosphere of comparatively even temperature.

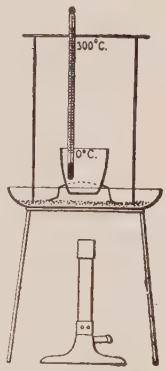

Fig. 299.

The sodium bicarbonate is converted to the carbonate. Constant weight will be obtained in about five or six hours. When the material no longer loses weight it is cooled in a desiccator and bottled for use, preferably in several small, glass-stoppered bottles. For exceedingly accurate work the material is analyzed and allowance made for the impurities that may still remain. The error caused by any such impurities is so small that for all practical purposes it may be neglected.

This purified sodium carbonate is an ultimate standard for acidimetric and alkalimetric volumetric analysis.

PREPARATION OF STANDARD ACID

STANDARD SULFURIC ACID

Fifty-two per cent sulfuric acid is in equilibrium with the average moisture present in the air of the laboratory; acid of this concentration is recommended for the standard stock solution.[3]

Pure 94 to 97% H_2SO_4 is diluted with sufficient water so that its gravity is about 1.4200 (42.7° Bé.). The acid is well mixed and poured into small clean and dry glass-stoppered sample bottles of about 200-ml. capacity. The bottles are carefully sealed and placed aside for use as desired. To determine the exact strength of this standard acid a portion is standardized against the sodium carbonate, prepared according to directions given.

Method of Standardization. Procedure.—(*a*) Direct. From a weighing bottle weigh out accurately about $40 \times N \times .053$ g. (where N is 1, 0.5, 0.1 etc. the approximate normality of the acid). Dissolve the sodium carbonate in 50 ml. distilled water, free of CO_2, and titrate using methyl orange indicator, or one of the mixed indicators (page 2192). For 0.1 N solutions a reference solution is prepared by adding the equivalent of $\frac{1}{2}$ drop of the standard acid to 100 ml. of water containing 2 drops of the indicator.

$$\frac{\text{Wt. of sodium carbonate}}{\text{Ml. of acid used in titration} \times .053} = \text{N of the acid.}$$

(*b*) Indirect. A catch weight of about 10 grams of the acid is weighed out in a weighing bottle or 100-ml. beaker (10 ml. = approximately 13 grams) and placed aside for titration. The amount of sulfuric acid in the sample (weight of sample multiplied by per cent divided by 100) is neutralized by 1.0808 times its weight of sodium carbonate. As an excess of acid is necessary to drive out all the carbonic acid the following formula is used—(grams H_2SO_4—0.05) $\times 1.0808$ = weight of Na_2CO_3 required.

The required amount of sodium carbonate is weighed and transferred to a 600-ml. Erlenmeyer flask and 100 ml. of water added. The acid is carefully poured into the flask and the rinsings of the weighing bottle or beaker added. The solution is boiled for 15 minutes to expel CO_2. A small filtering funnel inserted in the neck of the flask prevents loss during the boiling of the acid and carbonate mixture. The excess of acid is titrated with N/5 NaOH, using phenolphthalein indicator, the caustic being added drop by drop until a faint permanent pink color is obtained.

[3] Ninety-three thousand pounds of sulfuric acid, with an exposed surface of 1260 sq. ft. and depth of 10 in., had decreased in strength from 86% to 52.12% H_2SO_4, after standing in a lead pan, protected from the rain, for 42 days (Sept. 9th to Oct. 21st, 1916). Air was bubbled through a two-liter sample of this acid for seven consecutive days, when the solution was tested and found to contain 52.18% H_2SO_4. The average temperature of the laboratory was 74° F., the average vapor of the air (7 tests) was 0.2223 gram H_2O per standard cubic foot. The average humidity for September and October was 68%; the average temperature 62° F. The average humidity for the past 33 years was 72%; average temperature 57° F.

(The sulfuric equivalent to the NaOH added) + (weight of $Na_2CO_3 \times 0.9252$) = weight of pure H_2SO_4 present in the sample.

NOTES.—CO_2-free water should be taken in all titrations with phenolphthalein. The indicator contains 1 gram of the compound per liter of 95% alcohol. One ml. of indicator of this strength is required for each titration.

Results should agree to within 0.05%.

The temperature of the acid should be observed at the time of standardization and this noted with results on the bottles containing the standard samples. The coefficient of expansion is .00016+ per degree F. risen in temperature or .000293 per degree C. per ml. of solution.

Normal Sulfuric acid contains 49.043 grams of H_2SO_4 per liter of solution. To make a liter of the normal acid the amount of the standard acid required is calculated by the formula $\frac{100 \times 49.043}{\text{per cent } H_2SO_4 \text{ in standard}} = \text{grams standard acid}$ necessary. The acid is weighed out in a small beaker, a slight excess being taken (0.1 gram). The acid is washed into a liter flask and made to volume. An aliquot portion is standardized against the standard sodium carbonate. The solution may now be adjusted to the exact strength required.

Example.—If 25 ml. of the acid is found to contain 1.25 grams H_2SO_4 we find the amount of dilution required as follows: 25 ml. of N/1 H_2SO_4 should contain 1.226075 grams, therefore $1.226075 : 25 :: 1.25 : x$, and $x = \frac{25 \times 1.25}{1.226075}$. Then x minus 25 = the amount of water required for 25 ml. Total dilution = dilution for 25 multiplied by the volume of acid remaining in the flask divided by 25 = ml. water required to make a normal acid solution.

Fifth normal and tenth normal acids may be prepared by diluting the normal acid to five or ten volumes as the case requires.

Gravimetric Methods. Precipitation as $BaSO_4$.—Sulfuric acid may be standardized by precipitating as $BaSO_4$ according to the procedure given for sulfur. $BaSO_4 \times 0.4202 = H_2SO_4$.

Determination as $(NH_4)_2SO_4$.—To 10 ml. of the acid diluted to 50 ml. in a large platinum dish is added NH_4OH until the acid is neutralized and a faint odor of ammonia is perceptible. The solution is evaporated to dryness on the water bath and dried at 100° C. for half an hour. The residue is weighed as $(NH_4)_2SO_4$. $(NH_4)_2SO_4 \times 0.7422 = \text{gram } H_2SO_4$.

STANDARD HYDROCHLORIC ACID

Standard hydrochloric acid may be prepared from a solution of the acid containing a known amount of HCl. The stock solution, containing an exact amount of the HCl in solution, may be prepared by distilling dilute hydrochloric

acid until it has attained a definite boiling point. The pressure being known the exact amount of the acid that now distills and that remaining in the flask, provided the original solution was pure, can be estimated from the following table of Bonner and Wallace.[4]

Boiling Point Data of HCl

Press. Mm.	Boiling Pt.	Density, 25°	HCl %
600	102.209° C.	1.0980	20.638
640	103.967° C.	1.0973	20.507
680	105.564° C.	1.0968	20.413
700	106.424° C.	1.0966	20.360
740	107.859° C.	1.0962	20.268
760	108.584° C.	1.0959	20.222
800	110.007° C.	1.0955	20.155

Procedure.—The dilute acid, prepared from the solution of concentrated hydrochloric acid by diluting with an equal volume of distilled water, is placed in a flask of the distillation type with side arm. A thermometer is inserted and the acid heated to boiling. When a constant temperature is attained the distillate is caught for use. The barometric reading is taken at the time of distillation.

Acid of any strength desired can be prepared by direct measurement, the density and percentage of the acid being known from the table above. The density multiplied by the percentage of HCl and the result divided by 100 gives the weight of HCl per ml. of the stock solution.

Normal HCl contains 36.46 g. HCl per liter.

The weight of constant boiling HCl to weigh against brass weights in air to give 1 liter of N solution is given by Foulk and Hollingsworth.[5] The following will serve:

Barometer Reading when Acid was Collected	G. of Acid per 1 Liter of N Acid
770	180.407
760	180.193
750	179.979
740	179.766
730	179.555

Gravimetric Determination of Hydrochloric Acid by Precipitation as AgCl.—Hydrochloric acid may be standardized by precipitation with silver nitrate solution by the procedure for determination of chlorine. $AgCl \times 0.2544 = HCl$. It is advisable to heat the sample, diluted to a convenient volume, and add the hot silver nitrate in slight excess of that required by HCl, the amount of the reagent being calculated, e.g., mol. wt. HCl : mol. wt. $AgNO_3$ :: Wt. HCl in sample : x.

[4] W. D. Bonner and R. E. Wallace, Jour. Am. Chem. Soc., **52**, 1750 (1930).
[5] J. Am. Chem. Soc., **45**, 1220 (1923).

BENZOIC ACID STANDARD

Benzoic acid may be obtained in exceedingly pure form by melting the resublimed acid in a covered platinum dish in a constant-temperature oven, at a temperature of 140° C. The acid is poured into test-tubes, cooled, and the sticks bottled for use. The acid does not take up moisture to any appreciable extent, even when exposed to the air for some time, so that it may be weighed without danger of absorption of moisture.

STANDARD ALKALI SOLUTION

Standard normal sodium hydroxide is made by dissolving approximately 50 grams of NaOH sticks with 1 to 2 grams of $Ba(OH)_2$ in 200 to 300 ml. of water and diluting to 1000 ml. The caustic is standardized against normal or tenth normal hydrochloric or sulfuric acid, using phenolphthalein indicator. Other standard acids may be employed, such as oxalic, benzoic, and phthalic acids. See below. The solution is adjusted to the exact strength desired by addition of distilled water. The solution should be protected from CO_2 of the air—see Fig. 300, p. 2199.

NOTE.—The addition of $Ba(OH)_2$ is made to precipitate the carbonate in the caustic, as this would interfere with titrations in presence of phenolphthalein. As the presence of barium would produce a cloudiness with H_2SO_4 it is advisable to add only an amount sufficient to precipitate the carbonate. Milk of lime may be added in place of $Ba(OH)_2$.

Standardization of Sodium Hydroxide by Acid Potassium Phthalate.—Acid potassium phthalate, $KHC_8H_4O_4$, can be obtained in pure form. It has a high molecular weight, is not hygroscopic and may be weighed in an open container without danger of change. Phenolphthalein indicator is satisfactory for the titration.

Reaction: $KHC_8H_4O_4 + NaOH = KNaC_8H_4O_4 + H_2O$.

204.215 g. of the salt is equivalent to 1.008 g. H or 40 g. NaOH. 1.0211 g. is equivalent to 50 ml. of N/10 solution.

Procedure.—Weigh 2–5 grams of the acid potassium phthalate, transfer to a 300 ml. Erlenmeyer flask and dissolve in about 50 ml. of water. Add 3–4 drops of 1% phenolphthalein indicator and titrate with the NaOH solution to a faint pink color. (See note below.)

The normality of NaOH is obtained by dividing the volume equivalent of the acid potassium phthalate by the ml. NaOH. Volume equivalent = Wt. $KHC_8H_4O_4 \div 0.2042$ = ml. normal solution.

NOTE.—In a separate flask, with the same amount of solution and indicator, obtain the same color by adding NaOH drop by drop. Subtract this blank from the above titration before calculating normality.

Alkaline solutions that are to be used in presence of CO_2 are best standardized against standard acid solutions prepared by titration against Na_2CO_3 or against HCl prepared from the acid of constant boiling point, approximately 20.2% HCl.[6]

[6] G. A. Hulett and W. D. Bonner, J. Am. Chem. Soc., **31**, 390 (1909), and W. D. Bonner and R. E. Wallace, J. Am. Chem. Soc., **52**, 1750 (1930).

Precautions should be taken against the presence of CO_2 in the titrations where phenolphthalein is used. The distilled water should be freshly boiled, and the air in the flask should be free of CO_2.

Pure NaOH may be prepared by dissolving 100 grams of the pure stick NaOH in about 100 ml. of water, transferring to a large test tube and allowing to settle. If the solution is centrifuged for 20–30 minutes the sodium carbonate and other insoluble material will settle and the clear liquid may be used at once.[7] By means of a graduated pipette the required amount of the clear solution is drawn out and made to volume. 40 grams NaOH per liter is a normal solution. Other normalities may be desired. The NaOH should be kept in bottles lined with paraffine. This paraffining is done by heating the bottle, pouring in sufficient melted paraffine and rotating the bottle so that the paraffine flows over the sides and the entire inner surface.

The end-point with methyl orange indicator (3 drops 0.02% solution per 100 ml.) is the color obtained in a solution with pH = 4.2.

TO MAKE A SOLUTION OF APPROXIMATE NORMALITY STRENGTH WITHOUT WEIGHING, FROM A SOLUTION OF KNOWN STRENGTH AND SPECIFIC GRAVITY

Calculate the ml. of the reagent that contain the weight of the material necessary per liter. Measure out this volume and dilute to 1000 ml.

Example.—Required to make an approximate 0.1 N H_2SO_4 solution from 87% H_2SO_4 having a sp.gr. of 1.8.

A liter of normal solution contains 49.04 g. H_2SO_4, a 0.1 N 4.904 g. H_2SO_4. 1 ml. of the acid contains 1.8×0.87 g. H_2SO_4.

$$4.904 \text{ g. of } H_2SO_4 \text{ is present in } \frac{4.904}{1.8 \times 0.87} = 3.13 \text{ ml.}$$

Dilute 3.13 ml. of the acid to 1000 ml.

By using normal solutions of the acid or alkaline reagents the color changes of the indicators commonly employed are sharp. Lunge-Berl [8] regard 0.2 N solutions as the lower limit of concentration. It is occasionally advisable to use more dilute solutions even though the color changes are not so sharp.

Borax ($Na_2B_4O_7 \cdot 10H_2O$) is recommended by various investigators as a suitable ultimate standard for acid standardization, using methyl red as indicator, in 0.1 N titrations, or methyl orange if the reagent is stronger than 0.2 N.

In making up normal solutions it is necessary to note the temperature of the solution at the time of standardization, since a change of temperature will change the value of the reagent. The following corrections should be applied, the table taking the initial temperature to be 20° C.

15....0.00077		21....−0.00018
16....0.00064		22....−0.00038
17....0.00050	20....0.00000	23....−0.00059
18....0.00034		24....−0.00081
19....0.00018		25....−0.00103

The corrections apply to pure water. With the reagents indicated below the correction must be increased by the percentages indicated.

[7] Allen and Low, Ind. Eng. Chem., Anal. Ed., 5, 192 (1933).

[8] "Chemisch-Technische Untersuchungsmethodik," 7th Ed., Vol. I, p. 138.

N HNO_3 50%, HCl 25%, H_2SO_4 45%, NaOH 40%, KOH 40%, $H_2C_2O_4$ 30%, Na_2CO_3 40%.

N/10 HNO_3 6%, HCl 3%, H_2SO_4 5%, NaOH 5%, KOH 4%, $H_2C_2O_4$ 3%, Na_2CO_3 5%.

STANDARD BURETTES

Burettes used for this work should be carefully checked for accuracy of delivery.

For accurate titration of acids or alkalies it is advisable to have a titration of 75 to 100 ml. Since the straight 100-ml. burette if graduated to twentieths of a ml. would be too long for convenient handling, the chamber burette is used. The chamber located in the upper portion of the apparatus holds 75 ml., the lower portion drawn out into a uniform-bore tube is graduated in twentieths of a ml. Each tenth of a ml. has a mark passing entirely around the tube so that there will be no error in reading, the eye being held so that the mark appears to be a straight line drawn across the tube. The burette is enclosed in a large tube filled with distilled water and carrying a thermometer. The burette is connected, by means of an arm at the base, with a reservoir of standard acid. The cut, Fig. 300, shows the apparatus connected ready for use.

If vapor is lost from the standard reagents and this replaced by dry air, as in the common practice, the solution gradually changes in strength. A simple and ingenious device, designed by H. W. Herig (Gen. Chem. Co.), is shown at the top of Fig. 300, which overcomes this difficulty. The air drawn into the reagent bottle is purified and saturated with moisture by passing it through sodium hydroxide. A mercury valve relieves the pressure if expansion of air in the reagent bottle occurs due to rise of temperature.

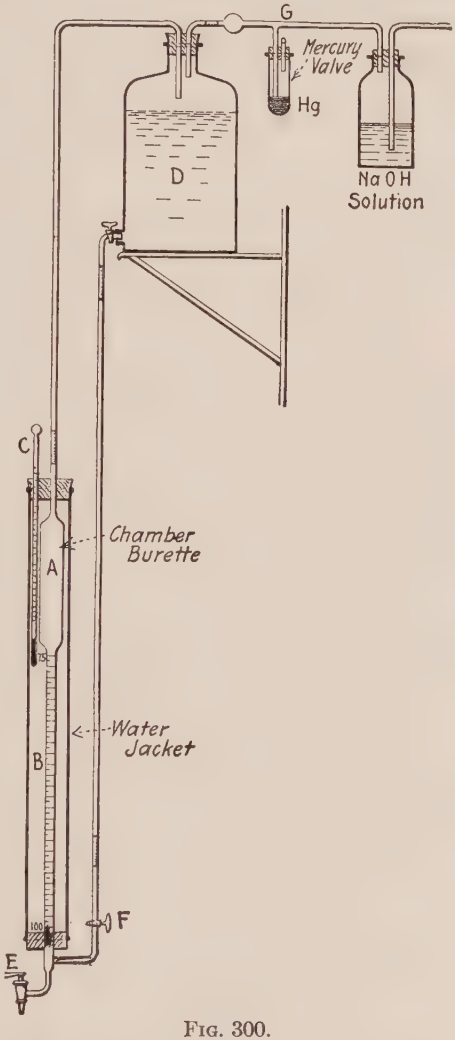

Fig. 300.

NOTE.—The chamber burette shown in Fig. 300 was designed at the Laurel Hill Laboratory, General Chemical Company.

TITRATION OF ACIDS AND ALKALIES

In the acid titration the sample is conveniently titrated in a white porcelain casserole. This gives a white background that enables the analyst to see the end-point. The caustic is run into the acid, to within a few ml. of the end-point, rapidly and then cautiously to a faint change of color—faint pink with phenolphthalein or an orange-yellow with methyl-orange. Phenolphthalein is generally preferred in acid titrations. CO_2-free caustic and water should always be used.

METHODS OF WEIGHING ACIDS

DILUTE ACIDS NON-VOLATILE UNDER ORDINARY CONDITIONS

Dilute acids may be weighed directly in a beaker, weighing bottle or ordinary pipette (see directions given later) by measuring out the approximate amount desired. Since a burette reading from 75-ml. to 100-ml. should be used for this work it will be necessary to take such an amount of the acid as will require a titration between these extremes. This may be accomplished by taking the specific gravity of the acid and referring to the table for the approximate strength. From this the volume necessary may readily be calculated.

Example.—The case will be taken where a 75-ml. to 100-ml. burette is being used and the titration is to be made with normal caustic solution; the acid titrated is sulfuric acid. The capacity of the burette is $75 \times 0.049 = 3.675$ grams H_2SO_4 to $100 \times 0.049 = 4.9$ grams H_2SO_4. (For HCl the capacity would be 2.74 to 3.65 grams HCl and for HNO_3 it would be 4.73 to 6.3 grams HNO_3.)

Suppose the sulfuric acid has a sp.gr. of 1.1600. From the table for H_2SO_4 we find that this acid is 22.25% H_2SO_4, then 1 ml. contains 1.16×22.25 divided by $100 = 0.2581$ gram H_2SO_4. Since the capacity of the burette is 3.675 to 4.9 grams H_2SO_4, we must weigh between 3.675 and 4.9 grams of the acid; to get this we should take $\frac{3.675}{.2581}$ to $\frac{4.9}{.2581}$ ml., that is to say, 14.5 to 18.5 ml. of the acid, which will weigh 16.8 grams to 21.5 grams.

WEIGHING CONCENTRATED ACIDS, FUMING OR VOLATILE UNDER ORDINARY CONDITIONS

The acid must be confined during weighing and until it is mixed with water or standard caustic. The best forms of apparatus include the following:

Lunge-Ray Pipette.—The pipette is shown in Fig. 301. Two glass stopcocks confine the acid in a bulb. The lower part of the pipette is protected by a ground-on test-tube. The dry pipette is weighed. Cock 2 is closed and 1 opened and a vacuum produced in the bulb by applying suction at the upper end of pipette and closing stopcock 1 with suction still on. The sample may now be drawn into the pipette by immersing the lower end in the sample and opening the stop-cock 2, the vacuum producing the suction. The increased weight = acid drawn in. The pipette is emptied by running the acid under water.

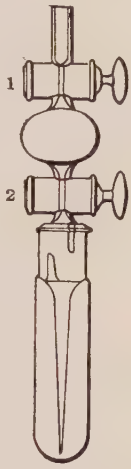

FIG. 301. Lunge-Ray Pipette.

Dely Weighing Tube.[9]—This form of weighing tube has proven to be of exceptional value, to the busy works-chemist, in the analysis of oleum and mixed acids. Both speed and accuracy are gained by its use. The apparatus, shown in Fig. 302, consists of a long glass tube of small bore, wound in a spiral coil.

The sample of acid is drawn into the weighed coil by applying suction through a rubber tube attached to *A* and drawing in the required amount of acid, a mark, ascertained by a previous run being made, to indicate the point to which the acid is drawn. The tip *B* is carefully wiped off with tissue paper and the tube and sample weighed. The weight of the tube deducted gives the weight of the sample.

The apparatus is now inclined so that the acid runs back into the crook at *C* to a point marked on the wall of the tube, in order to expel as much air as possible from this end. A rubber tube filled with water is attached to *A*, the other end of the rubber tube being connected to a bottle containing distilled water. A glass bead, such as is used in rubber-tipped burettes, fitting snugly in this tube, regulates the flow of water. The Dely tube is now inverted, the tip being immersed in 150 ml. to 200 ml. of distilled water in a 4-in. casserole—Fig. 302. By pressing gently on the bead, water is slowly admitted in the tube, forcing the acid before it. The acid and water are separated by a bubble of air. Before forcing out the last half-inch of acid, the tube connected to the water supply is disconnected and the weak acid from the casserole drawn back two or three inches into the Dely tube, then again the acid is almost entirely expelled by water from the reservoir and the procedure repeated. This is to absorb the SO_3 gas that invariably is present in the bubble of air above mentioned, which would be lost if forced out directly by the water column. In order to facilitate this last step it is well to have a short rubber tube attached to the Dely tube, and a glass tip in the

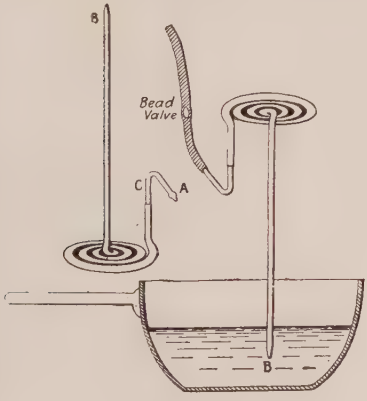

FIG. 302. Dely Weighing Tube in Operation.

[9] J. G. Dely, Chemist, Gen Chem. Co.

tube connected with the reservoir of water. The acid in the casserole, upon washing out the Dely tube, is titrated with standard caustic according to the procedure for titration of acids.

Fig. 303. Snake Tube.

The tube is dried after washing with alcohol, followed by ether, by heating on an asbestos mat on a hot plate, dry air being aspirated through.

Snake Weighing Tube.—The snake tube is a simple device that may be easily made by an amateur glass-blower. It is made out of a glass tube 8–10 ins. long, slightly thinner than a lead pencil. One end of the tube is drawn out to capillarity. The tube has a double bend, as shown in the illustration. It is so made that it rests on the double bend with the ends inclined upward to prevent the outflow of the acid. Fig. 303.

The tube is dried with alcohol, ether and air treatment, as in case of the Dely tube. After weighing the empty tube, acid is drawn into it by suction through an attached rubber tube. The capillary end that has dipped into the sample is wiped dry with tissue paper. The acid and tube are weighed and the acid estimated by difference.

The acid is run into 150 ml. of water in a casserole, the flow being regulated by the index finger pressed against the larger end of the tube. With careful regulation of the flow, practically no bumping occurs. With a small capillary opening it is not necessary to place the finger over the larger end of the tube as the acid flow will be slow. The tube should be kept in motion to prevent bumping from overheating any one portion. Kicking back of the acid indicates that the capillary end of the tube is too large. When the contents of the tube have run out, the tube is rinsed by sucking up some acid from the casserole and allowing it to run out, repeating several times. Suction may be applied by means of a rubber bulb attached to the tube. The acid is now titrated with standard caustic, using phenolphthalein indicator.

Blay-Burkhard Graduated Weighing Burette.[10]—This apparatus, designed by V. L. Blay and W. E. Burkhard, General Chemical Company, is used for weighing acids or other liquids. The form for general use is shown in Fig. 304. The burette is graduated in half ml. divi-

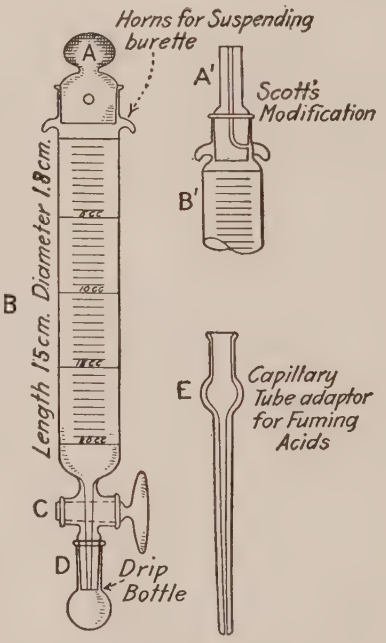

Fig. 304. Blay-Burkhard Graduated Weighing Burette.

[10] A similar burette of larger capacity and small weight was designed by Friedman and La Mer, Ind. Eng. Chem., Anal. Ed. **2**, 54 (1930).

sions, from 0 to 20 ml. An apparatus half this size is used for oleum, where a 2-ml. sample is sufficient for a determination. For the purpose of running the sample under water a capillary tube (*E*, Fig. 304), with ground joint, is attached to the burette. This tube is placed in the solution during titration. The burette is provided with a glass vented stopper (*A*) on the top, and a glass cap for the tip, both having ground joints, to prevent escape of fumes from the sample.

W. W. Scott modified the apparatus by replacing the fragile cap (*A*) by a tube stopper with capillary vent (see *A'*, Fig. 304). The vent to the air is opened or closed by a slight turn of this stopper. By means of this tube acid may be drawn into the burette according to the Lunge-Ray pipette procedure. With these burettes a man can control his work very accurately and save a great amount of time, both in weighing and manipulation.

In the analysis of strong oleum, about 50 grams of neutral Glauber salt are placed in a casserole containing water, and the fuming acid allowed to flow under the undissolved salt. The violent reaction of the acid with water is thus avoided. The tube *E*, Fig. 304, should be made of fused silica.

The glass-bulb method is still used for analysis of strong oleum. The acid weighed in a sealed tube of known weight is mixed with water by breaking the bulb in a stoppered bottle containing water, the acid is cooled and titrated as usual.

ANALYSIS OF MURIATIC ACID

(Commercial Hydrochloric Acid)

TOTAL ACIDITY AND HYDROCHLORIC ACID

The usual titration with standard caustic gives the total acidity, including, in addition to hydrochloric acid, nitric and sulfuric acids which may occur in the commercial product. The acidity due to these acids is deducted from the total acidity to find the actual HCl in the muriatic acid.

A catch weight, 10 to 15 grams of the acid, is weighed in a weighing bottle, or a large snake tube, or the Dely tube, as in case of oleum analysis, and the acid allowed to mix with water in a casserole; methyl-orange indicator is added and the acid titrated with standard normal caustic solution, the red color fading to a lemon-yellow. A fraction of a drop of the alkali will cause the change when the end-point has been reached.

One ml. N/1 NaOH = 0.03647 g. HCl.

NOTE.—Hydrochloric acid may be determined gravimetrically by precipitating the chloride with silver nitrate—$HCl + AgNO_3 = AgCl + HNO_3$, or by the volumetric methods for the determination of chlorine. See Chlorine.

DETERMINATION OF IMPURITIES IN COMMERCIAL HYDROCHLORIC ACID. FREE CHLORINE

Five ml. of the acid are diluted to 10 ml., about 5 ml. of fresh starch solution added and a few drops of 5% KI solution together with about 1 ml. of dilute H_2SO_4. A blue color indicates free chlorine. This color may be matched in a Nessler tube with a standard. It is possible to determine .0001% chlorine on a 5-ml. sample.

NITRIC ACID OR NITRATES IN HYDROCHLORIC ACID

About 5 ml. of the hydrochloric acid is cautiously added to 75 ml. of 95% H_2SO_4, the HCl being introduced under the surface of the sulfuric acid. The nitric acid may now be titrated with standard ferrous sulfate by the procedure for the direct determination of nitric acid and nitrates. (Method of Scott and Bowman.) The ferrous sulfate test for nitric acid is delicate. Traces of nitric acid produce a pink coloration; larger amounts a reddish brown to dark brown. The color is permanent when an excess of ferrous sulfate has been added.

SULFURIC ACID AND SULFATES IN HYDROCHLORIC ACID

Free H_2SO_4. Fifty ml. of the sample is evaporated in a platinum dish (steam bath) to dryness or until the HCl has been expelled. A few drops of water are added and the material again taken to dryness (steam bath). The residue is taken up with water and titrated with N/10 NaOH, using methyl-orange indicator. One ml. = 0.0049043 gram H_2SO_4.

Total Sulfates. Fifty ml. of the muriatic acid is evaporated to about 5 to 10 ml. and then diluted to about 200 ml. and heated to boiling. Total SO_3 is now precipitated by adding $BaCl_2$ solution as in case of determination of total sulfur. The precipitated $BaSO_4$ includes the free H_2SO_4 and the combined SO_3. $BaSO_4 \times 0.4202 = H_2SO_4$.

ARSENIC IN HYDROCHLORIC ACID

Commercial muriatic acid may contain arsenic. This is best determined by the Gutzeit Method given in detail under Arsenic. 10 ml. of sample is usually sufficient for this determination. If much arsenic is present the distillation method may be followed, using a 25 to 50-ml. sample. The distillate is titrated with standard iodine according to procedure given for arsenic by the iodine titration, page 99.

BARIUM CHLORIDE IN HYDROCHLORIC ACID

Fifty ml. is evaporated to dryness and then over a low flame to expel SO_3. The residue is taken up with 1 ml. of 1 : 1 HCl and 50 ml. of water. 1 ml. H_2SO_4 is added and the precipitated $BaSO_4$ filtered off and weighed. If silica is present in the sample its weight should be deducted. $BaSO_4 \times 0.8923 = BaCl_2$.

TOTAL SOLIDS AND SILICA

One hundred ml. of the HCl in a platinum dish is evaporated to dryness and the residue ignited and weighed. 5 ml. of HF is added with a few drops of H_2SO_4 and the solution again evaporated and ignited. *The first weight = total solids. The loss of weight in the second ignition = SiO_2.*

DETERMINATION OF SPECIFIC GRAVITY

Control tests for strength of the common inorganic acids are generally made in the plant by means of the hydrometer. This instrument depends on the fact that when a solid floats in a liquid, the weight of the liquid displaced is equal to the weight of the floating body. The hydrometer is a cylindrical instrument, generally with a spherical bulb, weighted with lead shot or mercury. It has a narrow stem with graduations, which indicate the gravity. The instrument floats vertically, after displacing its own weight of solution in which it is placed. The instruments are adapted for varying gravities extending over a range of ten to twenty divisions.

FIG. 305.—Hydrometer.

The Gravity tables given in the following pages have been developed with considerable care. By means of these one is able to obtain quickly and with fair degree of accuracy the strength of the acid or alkali of which the gravity is ascertained.

The following precautions should be observed in making hydrometer tests:

1. The hydrometer should be clean and dry, and at the temperature of the liquid, before immersing to make a reading.

2. The vessel in which the observation is made should be of clear glass of suitable size and shape, to allow the hydrometer to float freely (about $\frac{2}{3}$ inch greater in diameter than the hydrometer bulb) and of sufficient height to enable full reading of the hydrometer (*i.e.*, height greater than the length of the hydrometer).

3. The liquid should be thoroughly mixed by means of a stirrer reaching to the bottom of the vessel. There should be no air bubbles in the liquid or clinging to the sides of the vessel or the hydrometer.

4. The hydrometer is slowly immersed in the liquid, slightly beyond the point where it floats, and is then allowed to float freely.

5. The reading is made with the line of vision horizontal to the plane and as near as possible to this. The point is taken where this surface line cuts the hydrometer scale.

6. The temperature of the liquid is taken before and after the reading and allowance made for variation of the temperature from standard conditions as indicated in the tables.

References.—Cir. 16, 4th edition, Feb. 23, 1916, U. S. Bureau of Standards.
Sulfuric Acid Handbook by Thos. J. Sullivan, McGraw-Hill Book Co.
Thorpe Dictionary of Applied Chemistry, pp. 103–114. Longmans, Green and Co.

HYDROCHLORIC ACID

By W. C. Ferguson

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
1.00	1.0069	1.38	1.40	14.25	1.1090	21.80	21.68
2.00	1.0140	2.80	2.82	14.50	1.1111	22.22	22.09
3.00	1.0211	4.22	4.25	14.75	1.1132	22.64	22.50
4.00	1.0284	5.68	5.69	15.00	1.1154	23.08	22.92
5.00	1.0357	7.14	7.15	15.25	1.1176	23.52	23.33
5.25	1.0375	7.50	7.52	15.50	1.1197	23.94	23.75
5.50	1.0394	7.88	7.89	15.75	1.1219	24.38	24.16
5.75	1.0413	8.26	8.26	16.0	1.1240	24.80	24.57
6.00	1.0432	8.64	8.64	16.1	1.1248	24.96	24.73
6.25	1.0450	9.00	9.02	16.2	1.1256	25.12	24.90
6.50	1.0469	9.38	9.40	16.3	1.1265	25.30	25.06
6.75	1.0488	9.76	9 78	16.4	1.1274	25.48	25.23
7.00	1.0507	10.14	10.17	16.5	1.1283	25.66	25.39
7.25	1.0526	10.52	10.55	16.6	1.1292	25.84	25.56
7.50	1.0545	10.90	10.94	16.7	1.1301	26.02	25.72
7.75	1.0564	11.28	11.32	16.8	1.1310	26.20	25.89
8.00	1.0584	11.68	11.71	16.9	1.1319	26.38	26.05
8.25	1.0603	12.06	12.09	17.0	1.1328	26.56	26.22
8.50	1.0623	12.46	12.48	17.1	1.1336	26.72	26.39
8.75	1.0642	12.84	12.87	17.2	1.1345	26.90	26.56
9.00	1.0662	13.24	13.26	17.3	1.1354	27.08	26.73
9.25	1.0681	13.62	13.65	17.4	1.1363	27.26	26.90
9.50	1.0701	14.02	14.04	17.5	1.1372	27.44	27.07
9.75	1.0721	14.42	14.43	17.6	1.1381	27.62	27.24
10.00	1.0741	14.82	14.83	17.7	1.1390	27.80	27.41
10.25	1.0761	15.22	15.22	17.8	1.1399	27.98	27.58
10.50	1.0781	15.62	15.62	17.9	1.1408	28.16	27.75
10.75	1.0801	16.02	16.01	18.0	1.1417	28.34	27.92
11.00	1.0821	16.42	16.41	18.1	1.1426	28.52	28.09
11.25	1.0841	16.82	16.81	18.2	1.1435	28.70	28.26
11.50	1.0861	17.22	17.21	18.3	1.1444	28.88	28.44
11.75	1.0881	17.62	17.61	18.4	1.1453	29.06	28.61
12.00	1.0902	18.04	18.01	18.5	1.1462	29.24	28.78
12.25	1.0922	18 44	18.41	18.6	1.1471	29.42	28.95
12.50	1.0943	18.86	18.82	18.7	1.1480	29.60	29.13
12.75	1.0964	19.28	19.22	18.8	1.1489	29.78	29 30
13.00	1.0985	19.70	19.63	18.9	1.1498	29.96	29.48
13.25	1.1006	20.12	20.04	19.0	1.1508	30.16	29.65
13.50	1.1027	20.54	20.45	19.1	1.1517	30.34	29.83
13.75	1.1048	20.96	20.86	19.2	1.1526	30.52	30 00
14.00	1.1069	21.38	21.27	19.3	1.1535	30.70	30.18

HYDROCHLORIC ACID (Continued)

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
19.4	1.1544	30.88	30.35	22.5	1.1836	36.72	36.16
19.5	1.1554	31.08	30.53	22.6	1.1846	36.92	36.35
19.6	1.1563	31.26	30.71	22.7	1.1856	37.12	36.54
19.7	1.1572	31.44	30.90	22.8	1.1866	37.32	36.73
19.8	1.1581	31.62	31.08	22.9	1.1875	37.50	36.93
19.9	1.1590	31.80	31.27	23.0	1.1885	37.70	37.14
20.0	1.1600	32.00	31.45	23.1	1.1895	37.90	37.36
20.1	1.1609	32.18	31.64	23.2	1.1904	38.08	37.58
20.2	1.1619	32.38	31.82	23.3	1.1914	38.28	37.80
20.3	1.1628	32.56	32.01	23.4	1.1924	38.48	38.03
20.4	1.1637	32.74	32.19	23.5	1.1934	38.68	38.26
20.5	1.1647	32.94	32.38	23.6	1.1944	38.88	38.49
20.6	1.1656	33.12	32.56	23.7	1.1953	39.06	38.72
20.7	1.1666	33.32	32.75	23.8	1.1963	39.26	38.95
20.8	1.1675	33.50	32.93	23.9	1.1973	39.46	39.18
20.9	1.1684	33.68	33.12	24.0	1.1983	39.66	39.41
21.0	1.1694	33.88	33.31	24.1	1.1993	39.86	39.64
21.1	1.1703	34.06	33.50	24.2	1.2003	40.06	39.86
21.2	1.1713	34.26	33.69	24.3	1 2013	40.26	40.09
21.3	1.1722	34.44	33.88	24.4	1.2023	40.46	40.32
21.4	1.1732	34.64	34.07	24.5	1.2033	40.66	40.55
21.5	1.1741	34.82	34.26	24.6	1.2043	40.86	40.78
21.6	1.1751	35.02	34.45	24.7	1.2053	41.06	41.01
21.7	1.1760	35.20	34.64	24.8	1.2063	41.26	41.24
21.8	1.1770	35.40	34.83	24.9	1.2073	41.46	41.48
21.9	1.1779	35.58	35.02	25.0	1.2083	41.66	41.72
22.0	1.1789	35.78	35.21	25.1	1 2093	41.86	41.99
22.1	1.1798	35.96	35.40	25.2	1 2103	42.06	42.30
22.2	1.1808	36.16	35.59	25.3	1.2114	42.28	42.64
22.3	1.1817	36.34	35.78	25.4	1.2124	42.48	43.01
22.4	1.1827	36.54	35.97	25.5	1.2134	42.68	43.40

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 − 145/Sp. Gr.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

ALLOWANCE FOR TEMPERATURE:

10−15° Bé. — 1/40° Bé. or .0002 Sp. Gr. for 1° F.
15−22° Bé. — 1/30° Bé. or .0003 " " " 1° F.
22−25° Bé. — 1/28° Bé. or .00035 " " " 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
HENRY HOWARD, ARTHUR WYMAN,
A. G. ROSENGARTEN,
Executive Committee.

New York, May 14, 1903.

HYDROCHLORIC ACID

Specific Gravity. $\frac{15°}{4°}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.	Specific Gravity $\frac{15°}{4°}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.	Specific Gravity $\frac{15°}{4°}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.
1.000	0.16	1.6	1.075	15.16	163	1.145	28.61	328
1.005	1.15	12	1.080	16.15	174	1.150	29.57	340
1.010	2.14	22	1.085	17.13	186	1.152	29.95	345
1.015	3.12	32	1.090	18.11	197	1.155	30.55	353
1.020	4.13	42	1.095	19.06	209	1.160	31.52	366
1.025	5.15	53	1.100	20.01	220	1.163	32.10	373
1.030	6.15	64	1.105	20.97	232	1.165	32.49	379
1.035	7.15	74	1.110	21.92	243	1.170	33.46	392
1.040	8.16	85	1.115	22.86	255	1.171	33.65	394
1.045	9.16	96	1.120	23.82	267	1.175	34.42	404
1.050	10.17	107	1.125	24.78	278	1.180	35.39	418
1.055	11.18	118	1.130	25.75	291	1.185	36.31	430
1.060	12.19	129	1.135	26.70	303	1.190	37.23	443
1.065	13.19	141	1.140	27.66	315	1.195	38.16	456
1.070	14.17	152	1.1425	28.14	322	1.200	39.11	469

COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID*

Pressure mm. of Mercury.	Per Cent of HCl.	Grams constant boiling distillate for 1 mol. HCl.
770	20.218	180.390
760	20.242	180.170
750	20.266	179.960
740	20.290	179.745
730	20.314	179.530

Temperature of constant boiling hydrochloric acid is 108.54° at 763 mm. Specific gravity 1.09620^{25}.

* Hulett and Bonner, Jour. Am. Chem. Soc. xxxi, 390.

ANALYSIS OF HYDROFLUORIC ACID

The following constituents—hydrofluosilicic, sulfuric and sulfurous acids—commonly occurring with hydrofluoric acid, are determined in the analysis, along with the hydrofluoric acid, by titration. Generally the acid contains a slight residue upon ignition. The titrations are made in presence of KNO_3, first ice cold, and then completed at 80° C. or more. The cold titration gives the hydrofluoric, sulfuric and sulfurous acids and one-third of the hydrofluosilicic acid and upon heating the titration gives the remaining two-thirds of the H_2SiF_6, the following reactions taking place. Titration cold, $H_2SiF_6+2KNO_3 = K_2SiF_6+2HNO_3(=\frac{1}{3}\ H_2SiF_6)$. The liberated $2HNO_3$ requires 2NaOH. Titration hot, $K_2SiF_4+4NaOH = 4NaF+2KF+SiO_2+2H_2O(\frac{2}{3}\ H_2SiF_6)$.

The sulfuric acid is determined by titration with NaOH, upon expulsion of the accompanying more volatile acids. Sulfurous acid is determined by titration with standard iodine.

Special Apparatus.—***Chamber burette*** graduated from 75 to 100 ml. in 1/20 ml. as described under the determination of sulfuric acid, oleum, mixed acids, etc.

Platinum Weighing Tube.—Length about 5 cm., diameter 1.4 cm. The tube fitted with a platinum cap with a loop top to facilitate removal.

Brinton, Sarver and Stoppel found that the presence of silica in the NaOH causes an error in the titration, hence it is necessary to determine the SiO_2 in the NaOH and apply corrective factor if SiO_2 is present. Keep reagent in ceresin-lined bottles. If SiO_2 is present, the H_2SiF_6 will be too high and HF too low. Calculate the SiO_2 in one ml. of the reagent and the total SiO_2 in the total titration (cold) may now be obtained. Multiply the total SiO_2 by 2.393 (factor H_2SiO_3 divided by SiO_2) and deduct result from H_2SiF_6 obtained for true H_2SiF_6. Multiply the total SiO_2 by 1.991 (6HF divided by SiO_2) and add to the HF results for true HF content. Ref. Brinton, Sarver and Stoppel, Ind. Eng. Chem., **15**, 1880 (1923).

DETAILS OF PROCEDURE. TOTAL ACIDITY AND HYDROFLUOSILICIC ACID

A catch weight of the acid is taken by pouring the acid by means of the thief or directly from the paraffin bottle into the platinum weighing bottle, such a weight being taken as will require a titration of from 75 to 100 ml. of the normal caustic solution. (This may be judged by a preliminary run if the approximate value is not known.)

About 10 ml. of a saturated solution of KNO_3 is poured into a large platinum dish (capacity about 125 ml.), and chipped ice added. About 50 ml. of N/1 NaOH solution is run in from a burette and three drops of the strong phenolphthalein added. The platinum weighing bottle containing the sample is inverted beneath the surface of the caustic, the cover cautiously removed from the bottle by means of a heavy platinum wire, so as to allow the acid to mix very gradually with the standard NaOH (rapid addition is apt to cause loss of acid by fumes). Standard N/1 NaOH is added from the burette until the first permanent pink color is obtained. (The end-point will be uncertain and fading

unless the solution is kept cold—0° C.) The reading of the burette is noted—total $\frac{\text{N/1 NaOH}}{\text{Wt. of sample}} = \text{A}$. The dish is now placed on a hot plate and the solution warmed to about 80° C. and the titration completed with the N/1 NaOH solution to a permanent pink. Additional ml. required divided by weight of sample = B.

SULFURIC ACID IN HYDROFLUORIC ACID

About 5 grams of the sample are weighed in the platinum capsule and transferred to a large platinum dish, the capsule being rinsed out into the dish with water. The solution is evaporated on the steam bath to small volume (the evaporation is assisted by passing a hot current of pure dry air over the sample, see method on page 2233), a few drops of water are added and the evaporation repeated; no odor should be perceptible, all the hydrofluoric, hydrofluosilicic and sulfurous acids being expelled. The sulfuric acid is cooled, taken up with 100 ml. of CO_2-free water, three drops of strong phenolphthalein added and the acid titrated with N/1 NaOH solution in a 50-ml. burette. The ml. titration divided by the weight of the sample is noted as C. (See calculations at the close of the procedure.)

SULFUROUS ACID IN HYDROFLUORIC ACID

Ten grams of the sample are weighed in a tared platinum capsule with cover and washed into a large platinum dish with about 75 ml. of water. N/10 Iodine solution is added to a faint yellow. The end-point is made more distinct by addition of a little starch solution near the end of the reaction.

One ml. of N/10 I = 0.0041 g. H_2SO_3. ml. N/10 I ÷ wt. of sample = D.

Calculation of Results.

Factors. $H_2SO_4 \times 0.4904 = H_2SiF_6$.
$H_2SO_4 \times 0.4080 = HF$.
One ml. N/10 I = 0.0041 g. H_2SO_3.

Symbols. A = ml. NaOH for total acidity (cold) ÷ wt. of sample.
B = ml. of NaOH addition for H_2SiF_6 (hot) ÷ wt. of sample.
C = ml. NaOH for H_2SO_4 ÷ wt. of sample.
D = ml. N/10 iodine ÷ wt. of sample.

Formulae for Calculation.—If E = value of 1 ml. of the standard N/1 caustic in terms of H_2SO_4 then

$$\text{Per cent HF} = \left(\text{A} - \frac{\text{B}}{2} - \text{C}\right) \times \text{E} \times 0.408 \times 100 - 0.2\text{D};$$

$$\text{Per cent } H_2SiF_6 = \frac{3}{2}\text{B} \times \text{E} \times 0.4904 \times 100;$$

$$\text{Per cent } H_2SO_4 = \text{C} \times \text{E} \times 100;$$

$$\text{Per cent } H_2SO_3 = \text{D} \times 0.0041 \times 100.$$

Residue.—This is determined by evaporation of 15 to 20 grams of the acid in a platinum dish, and gentle ignition of the dry residue.

NOTES AND PRECAUTIONS.—Weighings should be made quickly in covered platinum weighing bottles.

It is advisable to weigh out the sample for the sulfuric acid determination first and start the evaporation to facilitate more rapid results.

Iodine is preferred to permanganate for titration of H_2SO_3 as the latter also titrates organic matter that is apt to occur in the acid.

COMPLETE ANALYSIS OF NITRIC ACID

The acidity of nitric acid obtained by titration with standard caustic may be due not only to HNO_3 but to impurities H_2SO_4, HCl and lower oxides of nitrogen, hence for extremely accurate analysis it is essential to look for these impurities and make allowances accordingly if they are found to be present. Nitric acid may be determined directly by titration with ferrous sulfate according to the procedure given in detail, page 2214; this titration will include combined nitrates as well as the free acid, whereas the titration with caustic includes only free acids. In addition to the above-mentioned impurities, commercial nitric acid frequently contains free chlorine, chlorides, chlorates, iodine, iodides, iodates, silica, and suspended solids; the last is reported as insoluble residue. In an analysis of nitric acid the impurities, which are known to be injurious to the art for which the acid is used, are looked for and determined if present.

DETERMINATION OF TOTAL ACIDITY

As in case of mixed acids and, in fact, all accurate determinations of acids with caustic, such an amount of the sample should be taken as will require a titration within the limits of the standard chamber burette—75 to 100 ml. For normal caustic this would require 4.726 to 6.3 grams of 100% HNO_3 or a fifth or tenth of this amount for N/5 or N/10 NaOH. From the specific gravity of the acid its approximate strength can be obtained by referring to the table for nitric acid and calculating the volume and approximate weight required for analysis (see example under Methods of Weighing Acids—Dilute Acids—Non-Volatile under Ordinary Conditions, page 2200).

The acid is weighed in a weighing bottle, or in the Dely tube or Blay-Burkhard pipette, if it is a fuming acid. The titration is made in a casserole, the acid being mixed with 150 to 200 ml. of CO_2 free water and titrated in presence of phenolphthalein indicator. (Methyl-orange is destroyed by nitrous acid.) The total acidity is expressed in terms of H_2SO_4 if other acids are present.

$$\frac{\text{ml. N/1 NaOH} \times .049043 \times 100}{\text{Weight of the sample}} = \text{per cent } H_2SO_4 \text{ equivalent.} \quad H_2SO_4 \times 1.285 = HNO_3.$$

Direct calculation to HNO_3 $\frac{\text{ml. N/1 NaOH} \times 0.063018 \times 100}{\text{Weight of the sample}} = \text{per cent } HNO_3.$

DETERMINATION OF SULFURIC ACID IN NITRIC ACID

About 10 grams of the acid are evaporated to dryness on the steam bath. The residue is taken up with about 10 ml. of water and the evaporation repeated until free from nitric fumes, the residue finally diluted to 100 ml. and the sulfuric acid titrated with N/5 NaOH, using phenolphthalein or methyl-orange indicator. Gravimetrically the acid may be precipitated from a hot solution as $BaSO_4$ by addition of barium chloride reagent according to the method for determining sulfur.

One ml. N/5 NaOH = 0.009809 gram H_2SO_4.

$BaSO_4 \times 0.4202 = H_2SO_4$. Per cent = 100 divided by weight of sample $\times H_2SO_4$ obtained.

DETERMINATION OF HYDROCHLORIC ACID IN NITRIC ACID

A 5- to 50-gram sample is taken, that is to say, a sufficient amount of the acid so that a weighable amount of AgCl may be obtained. The sample is nearly neutralized with NH_4OH (it should be slightly acid with HNO_3) and a slight excess of silver nitrate reagent added to the hot solution; the mixture is stirred thoroughly, then allowed to settle for one or two hours. The AgCl is filtered through a weighed Gooch crucible containing an asbestos mat, then washed, dried and ignited at 130–150° C. (See general method for the determination of chlorine.)

Factors. $AgCl \times 0.2474 = Cl$. $AgCl \times 0.2544 = HCl$.
$AgCl \times 0.34212 =$ equivalent H_2SO_4.

Find the per cent HCl and the per cent equivalent H_2SO_4.

LOWER OXIDES. DETERMINED AS NITROUS ACID

For practical purposes the lower oxides of nitrogen that may be present in nitric acid are calculated to N_2O_3 or HNO_2. If it is desired to report these as N_2O_4 the conversion factor given below may be used. The lower oxides may be obtained by titration with standard permanganate, other reducing agents being absent. In presence of organic matter titration with standard iodine solution should be made. (See general procedure for determination of nitrous acid, etc.)

It makes but little difference whether the permanganate is added to the sample containing nitrite or the sample added to a measured amount of per-

manganate, provided in the first method the titration be made as rapidly as possible to prevent oxidation taking place due to dilution of the sample with water. The end-point in the first procedure is quicker and sharper.

Potassium permanganate oxidizes nitrous acid to nitric according to the reaction $2KMnO_4+5HNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5HNO_3+3H_2O$. Therefore 1 ml. of N/1 $KMnO_4=0.02351$ gram HNO_2 or 0.019 gram N_2O_3.

Twenty-five ml. of the acid are diluted in a casserole to about 300 ml. with cold water, and 25 ml. of dilute H_2SO_4, 1 : 4 added. The solution is titrated immediately with N/5 $KMnO_4$, the reagent being added rapidly at first and finally drop by drop as the end-point is approached. The reaction near the end is apt to be slow, so that time must be allowed for complete oxidation. The titration is completed when a pink color is obtained, that persists for three minutes.

$$\text{ml. N/5 } KMnO_4 \times 0.004702 = \text{gram } HNO_2.$$

The result multiplied by $\frac{100}{\text{wt. sample}}$ = per cent.

$$HNO_2 \times 1.0431 = \text{equivalent } H_2SO_4.$$

NITRIC ACID

From the total acidity expressed as H_2SO_4 is subtracted the acidity due to HCl and HNO_2 (lower oxides of nitrogen) expressed in terms of H_2SO_4. The remainder is due to nitric acid, in terms of sulfuric acid.

$$H_2SO_4 \times 1.285 = HNO_3.$$

DETERMINATION OF IODINE IN NITRIC ACID

Fifty ml. of the acid in an Erlenmeyer flask is neutralized with caustic, the mixture being cooled in running water during the operation. The solution, poured into a separatory funnel, is made acid with dilute H_2SO_4 and a few drops of 1% solution of KNO_2 added, followed by about 25 ml. of CS_2 or CCl_4. The mixture is shaken to extract the free iodine and the CS_2 or CCl_4 drawn off and the extraction repeated by addition of KNO_2 and CS_2 or CCl_4 until all the iodine has been extracted. Iodine present as iodide is extracted by this method. To obtain the iodine from iodate, H_2S water is added and the extraction with addition of $NaNO_2$ and CS_2 repeated.

The combined extracts are washed in a separatory funnel until free of acid. The iodine is now titrated with standard sodium thiosulfate by adding 25 to 30 ml. of water together with 5 ml. of 1% sodium bicarbonate solution (10 grams $NaHCO_3$ per liter + 1 ml. HCl).

$$\text{One ml. N/10 } Na_2S_2O_3 = 0.01269 \text{ gram I.}$$

Reactions.

$$2HI+2KNO_2+H_2SO_4=K_2SO_4+2H_2O+I_2+2NO;$$
$$2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6.$$

DETERMINATION OF FREE CHLORINE IN NITRIC ACID

When a current of pure air is passed into nitric acid containing free chlorine the air blows out the chlorine. If air aspirated through a sample of nitric acid is passed through a solution of potassium iodide the free chlorine will displace the iodine. The liberated iodine may now be titrated with standard sodium thiosulfate and the equivalent chlorine calculated.

TOTAL NON-VOLATILE SOLIDS

These may be determined by evaporating a large sample of 100 to 200 ml. of the nitric acid to dryness. The residue is heated gently to expel the last traces of nitric acid and then washed into a platinum dish, again evaporated to dryness and ignited to a dull red heat. The residue is due to non-volatile solids.

FERROUS SULFATE METHOD FOR THE DIRECT DETERMINATION OF NITRIC ACID [11]

Although the test for nitric acid by ferrous sulfate in presence of conc. sulfuric acid has long been known, the reagent has not been used for an accurate quantitative method until F. C. Bowman and W. W. Scott developed the procedure herein given. Nitric acid may be determined quantitatively in arsenic acid by titration with ferrous sulfate containing free sulfuric acid. The method is also applicable to the determination of nitric acid in phosphoric acid and in sulfuric acid, including oleums and mixed acids. The reaction in phosphoric acid and arsenic acid goes further than it does in sulfuric acid. The following equations represent the reactions taking place:

Reaction in Arsenic or Phosphoric Acids:

$$6FeSO_4+2HNO_3+3H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O.$$

Reaction in Sulfuric Acid:

$$4FeSO_4+2HNO_3+2H_2SO_4=2Fe_2(SO_4)_3+N_2O_3+3H_2O.$$

Oxidizing agents such as chlorates, iodates, bromates, etc., interfere, owing to their oxidizing action on ferrous sulfate, hence these should be absent from the sample or allowance made, if appreciable amounts are present. NaCl up to 0.002 gram does not interfere; larger amounts tend to lower results. KI and KBr react in a similar manner to NaCl, 0.002 gram causing no interference. KNO_2 present in amounts up to 50% of the HNO_3 does not interfere. The sample should not contain over 25% water, nor should the temperature exceed 60° C. during titration. 0.1 to 0.8 gram HNO_3 are accurately titrated, in sulfuric acid.

[11] J. Ind. Eng. Chem., **7**, 766 (1915).

Special Reagents Required. *Standard Ferrous Sulfate.*

A. Reagent to be Used in Titration of Nitric Acid in Sulfuric Acid, Oleum, etc.—176.5 grams of $FeSO_4 \cdot 7H_2O$ are dissolved in about 400 ml. of water, and 500 ml. of about 60% H_2SO_4 (1 vol. 66° Bé. acid per 1 vol. H_2O) are added with constant stirring, and the solution (cooled if necessary) made up to 1000 ml. 1 ml. will be equivalent to 0.02±gram HNO_3, the exact value being determined by standardization.

B. Reagent for Titration of Nitric in Phosphoric or Arsenic Acid.—Ferrous sulfate to be used should be made up as follows: 264.7 grams of $FeSO_4 \cdot 7H_2O$ is dissolved in 500 ml. of water, 50 ml. of 66° Bé. H_2SO_4 (93.2%), added and the solution made up to 1000 ml. 1 ml. will be equal to approximately 0.02 gram HNO_3. The exact strength is ascertained by titrating a known amount of nitric acid in phosphoric or arsenic acid upon warming to 40° or 50° C.

Standard Nitric Acid.—The acid should contain about 40 grams of HNO_3 (100%) per liter of solution, e.g., 41 ml. of the desk reagent (sp.gr. 1.42) per liter will give the strength desired, the exact value being determined by titration of the acid against standard caustic.

Potassium Dichromate, N/2 $K_2Cr_2O_7$ Solution.—The exact value in terms of iron should be known.

STANDARDIZATION OF FERROUS SULFATE REAGENT

1. Titration against Standard Nitric Acid.

A. Reagent to be Used for Determination of Nitric in Sulfuric Acid.—Ten milliliters of the standard $HNO_3 = 0.4 \pm$g. (the exact amount having been ascertained) is run into 100 ml. of 66° Bé. (93.2%) H_2SO_4, free from oxidizing agents (HNO_3, etc.) and the resulting mixture titrated with the standard $FeSO_4$ solution according to the directions given under the General Procedure for determining HNO_3 in H_2SO_4, page 2217.

Weight of HNO_3 taken divided by ml. of $FeSO_4$ minus 0.2 ml.[12] = grams HNO_3 ml. $FeSO_4$.

B. Standardization of the Reagent Used in the Determination of Nitric in Arsenic and Phosphoric Acids.—Ten milliliters of the standard $HNO_3 = 0.4 \pm$gram (the exact amount having been ascertained) is run into 100 ml. of H_2AsO_4, or H_3PO_4, according to the product to be titrated, the mixture warmed and titrated according to directions given under Procedure for determination of HNO_3 in arsenic or phosphoric acid.

Weight of HNO_3 taken, divided by ml. $FeSO_4$ = grams HNO_3 per ml. $FeSO_4$.

2. Standardizing Ferrous Sulfate with Standard Potassium Dichromate.

A. Reagent to be Used in Determination of Nitric in Sulfuric Acid.—Twenty-five milliliters of N/2 $K_2Cr_2O_7$ (or 125 milliliters N/10 $K_2Cr_2O_7$) are accurately measured out into a 250-ml. beaker and the solution titrated with the $FeSO_4$ reagent, until the first fraction of a drop of excess produces a blue color with potassium ferricyanide indicator on a spot plate. Usually between 19 to 20 ml. are required. The iron value of the dichromate multiplied by 0.5643 = gram HNO_3 for the total ml. of $FeSO_4$ required in the titration.

[12] An excess of 0.2 ml. $FeSO_4$ is required to produce the desired color reaction in 100 ml. of pure H_2SO_4.

Calculation.

Since N/2 $K_2Cr_2O_7$ = 0.024517 gram salt, 1 gram $K_2Cr_2O_7$ = 1.13882 Fe, therefore 25 ml. = 0.024517 × 1.13882 × 0.5643 × 25 = 0.3939 gram HNO_3 equivalent.

0.3939 divided by ml. $FeSO_4$ required in the titration = grams HNO_3 equivalent per ml.

B. Reagent to be Used in Determination of HNO_3 in H_3AsO_4 or H_3PO_4.—Thirty-eight milliliters of $K_2Cr_2O_7$ solution are titrated with $FeSO_4$ according to directions given in "A." The Fe value multiplied by 0.3762 = gram HNO_3.

Calculation.—Thirty-eight milliliters of $K_2Cr_2O_7$ = 0.024517 × 1.13882 × 0.3762 × 38 = 0.3991 gram HNO_3 equivalent. 0.3991 divided by ml. $FeSO_4$ required in the titration = grams HNO_3 equivalent per ml.

Factors.

$K_2Cr_2O_7$ to Fe = 1.13882, reciprocal = 0.8781.

2Fe to HNO_3 = 0.5643, recip. = 1.7722. 3Fe to HNO_3 = 0.3762, recip. = 2.6582.

HNO_3 to $2FeSO_4 \cdot 7H_2O$ = 8.8235 recip. = 0.1133.

HNO_3 to $3FeSO_4 \cdot 7H_2O$ = 13.2348, recip. = 0.07556.

$K_2Cr_2O_7$ to HNO_3 = 0.6426, recip. = 1.5562. (Titration of A reagent.)

$K_2Cr_2O_7$ to HNO_3 = 0.4284, recip. = 2.3342. (Titration of B reagent.)

GENERAL PROCEDURE. DETERMINATION OF NITRIC ACID IN SULFURIC ACID

The procedure is applicable to the determination of nitric acid, free or combined as nitrate, sulfuric acid being used as the medium in which the titration is made. Although 0.1 to 0.8 gram HNO_3 may be accurately titrated, it is a general practice to have the nitric acid content of the sample taken for the titration about the same as the amount taken in standardization of the $FeSO_4$ reagent. A preliminary run on the original material is made, if the approximate nitric acid content is not known. Solids are dissolved in water and made to the desired volume, strong HNO_3 is diluted with water. In either case the dilution should be such that 10 ml. of the solution will contain approximately 0.4 gram HNO_3. Mixed acids and oleum containing over 10% HNO_3 should be mixed with additional 66° Bé. (93+per cent H_2SO_4) and made to a definite volume, an aliquot part being taken for titration.

EVALUATION OF NITRIC ACID OR NITRATES

If the nitric acid is known to be free of other acids it may be titrated directly with caustic; combined nitrate cannot be titrated with caustic, but may be accurately determined by the ferrous sulfate method. The approximate strength of the HNO_3 or salt having been determined on 1 ml. or 1 gram sample (if the material is a solid), the requisite amount is weighed and made to volume, 10 ml. of which should contain not more than 0.8 gram or less than 0.1 gram HNO_3, preferably about 0.4 gram.

Example.—Suppose 1 ml. required a titration of 43.8 ml. $FeSO_4$, 10 ml. would require a titration of 438 ml., whereas 20 ml. is desired. 438 divided by 20 = approximately 22, e.g., the dilution should be to 22 volumes. 23 ml.

of the solution diluted to 500 ml. will give a mixture of the desired strength. 23 ml. are accordingly weighed in a weighing bottle, the acid washed into a beaker transferred then to the graduated 500-ml. flask and made to volume. The preliminary run may be made in two or three minutes.

Titration.—A 250-ml. beaker containing 100 ml. of concentrated, nitric free, H_2SO_4 (93+%) is placed in a large casserole or deep porcelain dish containing cold water. 10 ml. of the sample are measured out in an accurately marked pipette, graduated to contain exactly 10 ml. The solution is run under the surface of the sulfuric acid, the delivery tip of the pipette being kept in constant circular motion to prevent too much local heating. Since the sides of the beaker are cooled, the tip of the pipette should be kept against the sides in the circular sweep during the delivery. By this procedure loss of nitric acid is reduced to the minimum.

The ferrous sulfate solution is now added from a burette in a fine stream until the yellow color that first forms takes on a faint brownish tinge (dirty yellow). The pipette is now rinsed out by sucking up the mixture and draining it back into the beaker. The titration is now completed, adding the $FeSO_4$ cautiously drop by drop until the yellowish brown color again appears, a drop in excess producing an appreciable darkening of the solution. A larger excess produces a brownish red color. With small amounts of HNO_3 a pink color will be obtained, instead of the yellowish brown. The end-point once recognized is readily duplicated.

Calculation.—The ml. titration minus the blank 0.2 ml. multiplied by the factor for $FeSO_4$ = weight of HNO_3. $HNO_3 \times 100 \div$ wt. = per cent.

Example.—Suppose 10 ml. equivalent to 1/50 of a 42-g. sample weighed, requires 22 ml. $FeSO_4$ whose value = 0.02 g. HNO_3 per ml., then $(0.44 \times 100)/0.84 = 52.4\%$ HNO_3.

DETERMINATION OF NITRIC ACID IN OLEUM OR IN MIXED ACIDS. FERROUS SULFATE METHOD

The rapidity and accuracy of the method for determining HNO_3 in sulfuric acid makes it valuable for determining nitric acid in oleums and mixed acids. Nitrated oleums may be weighed and titrated without diluting to definite volume. Mixed acids containing large percentages of nitric acid, however, require dilution with H_2SO_4, as stated under General Procedure.

Procedure.—The sample may be weighed in a Dely weighing tube (see analysis of oleum and mixed acids), or in a standard pipette (5 ml. generally taken = 9.61 grams). If the latter is used, the sample is sucked into the pipette, a rubber tube, with glass bead valve, being attached to the upper end, to which suction is applied without danger of drawing SO_3 fumes into the mouth. A little vaseline placed on the tip of the pipette prevents loss of acid during the weighing. In routine analysis, where a large number of daily samples of oleum are analyzed, and the specific gravity of the oleum does not vary appreciably, 5- to 10-ml. samples may be drawn out, by means of a pipette, and titrated without weighing, the weight being calculated from the gravity.

The acid is run under cold concentrated H_2SO_4 (93%), and titrated accord-

ing to directions under General Procedure for Nitric Acid. A blank of 0.2 ml.[13] having been deducted, ml. $FeSO_4 \times HNO_3$ factor for $FeSO_4 \times 100$ divided by wt. taken = per cent HNO_3.

Correction Factor.—In making a number of runs with varying amounts of HNO_3, it was found that small quantities of nitric acid required a proportionally greater amount of $FeSO_4$ than larger quantities of HNO_3. For example, 0.07392 gram HNO_3 required 3.9 ml. $FeSO_4$, four times the amount of HNO_3 required 15 ml. $FeSO_4$, in place of 15.6 (3.9×4), and six times 0.07392 gram HNO_3 required 22.5 ml. $FeSO_4$ in place of 23.4. It was observed that even traces of HNO_3 required a titration of over 0.2 ml. It is evident that a deduction of 0.2 ml. makes the titrations multiples of the lowest, e.g., 3.7, 14.8 and 22.3. Again it was found that standardization of $FeSO_4$ with HNO_3 checked the dichromate factor when 0.2 ml. was deducted from the first series of titrations. This led to the conclusion that a constant blank of 0.2 ml. should be deducted from the ferrous sulfate titrations of nitric acid in presence of 100 ml. of nitric free sulfuric acid (66° Bé.).

Comparison of results:
$FeSO_4$ value by HNO_3 corrected = 0.02067 gram. Uncorrected = 0.02045 gram HNO_3.
$FeSO_4$ value by $K_2Cr_2O_7$ titration = 0.02083 gram HNO_3.

Accuracy of the Ferrous Sulfate Method.—Results obtained by the ferrous sulfate method agree closely with those obtained by the nitrometer. The following data were obtained by Mr. B. S. Clark, by the $FeSO_4$ method, on nitrated oleums. The figures below the first row are checks obtained on these samples by purchasers of the acid, the nitrometer method being used.

$FeSO_4$ method.	2.40; 2.82; 3.23; 3.35; 3.52; 3.50; 3.48; 3.57; 3.53; 3.56.
Nitrometer method.	2.35; 2.79; 3.26; 3.39; 3.57; 3.53; 3.50; 3.58; 3.57; 3.56.
Difference.	0.05; 0.03; 0.03; 0.04; 0.05; 0.03; 0.02; 0.01; 0.04; 0.00.

DETERMINATION OF NITRIC ACID IN ARSENIC AND PHOSPHORIC ACIDS BY THE FERROUS SULFATE METHOD

A direct procedure for the determination of nitric acid in arsenic acid or phosphoric acid has been sought on account of the inaccuracy of the evaporation method, since it is difficult to completely expel HNO_3 from these acids. Ferrous sulfate, in presence of sulfuric acid, quantitatively titrates nitric in arsenic acid, the following reaction taking place:

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 + xH_3AsO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O + xH_3AsO_4.$$

The procedure is applicable to the determination of nitric acid in phosphoric acid, the end-point being sharper in this acid than in arsenic. The procedure gives very excellent results in either acid and is recommended for accuracy and rapidity.

[13] Back titrations of the excess of $FeSO_4$ may be made with standard $K_2Cr_2O_7$, using the ferricyanide spot test for ferrous iron.

Sp.gr. of twelve average samples of oleum had a difference of only 0.01. 5 ml. weighs 9.61 grams. This is found convenient for analysis. 10 ml. = 19.22 grams will usually give a titration of about 20+ml. on the usual nitrated oleum.

Standardization of Ferrous Sulfate has already been given under special reagents. It must be remembered that the arsenic or phosphoric acid diluents should be free from nitric acid or the blank on 100 ml. be ascertained and deducted from titrations made in this diluent.

Procedure.—The amount of the sample to be taken is governed by the nitric acid present as an impurity. This may be quickly determined by a preliminary run on a 10-ml. sample, the diluent being the same acid (HNO_3 free) as the acid titrated.

Example.—Suppose 10 ml. require a titration of 4.5 ml. of $FeSO_4$, whereas a titration of 20 ml. is desired, then $20 \times 10 \div 4.5 = 44.44$ ml. of the sample required.

The required amount of the acid is measured out and weighed, if its sp.gr. is not known. The acid is poured into a 4-in. casserole and diluted with 100 ml. of nitric free acid of the same kind as that being titrated. The mixture is gently warmed to 40 to 50° C. and titrated with standard ferrous sulfate reagent to a permanent yellowish brown. Towards the end of the titration the acid will boil with each addition of the $FeSO_4$ and the characteristic reddish yellow fumes will be given off. (This does not occur in titrations of HNO_3 in H_2SO_4.)

When very small amounts of nitric acid are present it is often necessary to add a known amount of HNO_3 to start the reaction. The titration in excess of that required by the added HNO_3 is due to the nitric acid in the sample. Very small amounts of HNO_3 produce a pink color.

Calculation ml. $FeSO_4 \times HNO_3$ factor for $FeSO_4 \times 100$ divided by weight taken = % HNO_3.

Factors. Fe to $HNO_3 = 0.3762$. Reciprocal = 2.6582.

Note.—In a 20-gram sample 1 ml. 0.02 reagent = 0.1% per ml.

DETERMINATION OF NITROUS ACID OR NITRITE

PERMANGANATE METHOD

Principle.—Potassium permanganate reacts with nitrous acid or a nitrite as follows:

$$5N_2O_3 + 4KMnO_4 + 6H_2SO_4 = 5N_2O_5 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$
$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

Details of the general procedure for nitrites is given on page 653, Vol. I. Nitrous acid in nitric acid may be determined as stated on page 2212. Lower oxides of nitrogen in mixed acids are determined as outlined on page 2234.

NITRIC ACID

By W. C. Ferguson

Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.	Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.
10 00	1.0741	14.82	12.86	21.25	1.1718	34 36	28.02
10.25	1 0761	15.22	13.18	21.50	1.1741	34.82	28.36
10.50	1.0781	15.62	13.49	21.75	1.1765	35.30	28.72
10.75	1.0801	16.02	13.81	22.00	1.1789	35.78	29.07
11.00	1.0821	16.42	14.13	22.25	1.1813	36 26	29.43
11.25	1.0841	16.82	14.44	22.50	1.1837	36.74	29 78
11.50	1.0861	17.22	14.76	22.75	1.1861	37.22	30.14
11.75	1.0881	17 62	15 07	23.00	1.1885	37.70	30 49
12.00	1.0902	18 04	15 41	23.25	1.1910	38.20	30.86
12.25	1.0922	18.44	15.72	23.50	1.1934	38.68	31 21
12.50	1.0943	18 86	16.05	23.75	1.1959	39.18	31.58
12.75	1.0964	19 28	16.39	24.00	1.1983	39.66	31.94
13.00	1.0985	19 70	16.72	24.25	1.2008	40.16	32.31
13.25	1.1006	20 12	17.05	24.50	1.2033	40 66	32.68
13.50	1.1027	20.54	17 38	24.75	1 2058	41.16	33 05
13.75	1.1048	20 96	17.71	25 00	1.2083	41.66	33.42
14.00	1.1069	21.38	18 04	25.25	1.2109	42.18	33.80
14.25	1.1090	21.80	18 37	25.50	1 2134	42 68	34 17
14.50	1.1111	22.22	18.70	25.75	1 2160	43.20	34.56
14.75	1.1132	22.64	19.02	26.00	1 2185	43.70	34.94
15.00	1.1154	23.08	19 36	26.25	1.2211	44.22	35.33
15.25	1.1176	23.52	19.70	26.50	1.2236	44.72	35.70
15.50	1.1197	23.94	20.02	26.75	1.2262	45.24	36 09
15.75	1.1219	24.38	20.36	27.00	1.2288	45.76	36.48
16.00	1.1240	24 80	20.69	27.25	1.2314	46.28	36 87
16.25	1.1262	25.24	21.03	27.50	1.2340	46.80	37 26
16.50	1.1284	25.68	21 36	27.75	1 2367	47.34	37.67
16.75	1.1306	26.12	21.70	28.00	1.2393	47.86	38 06
17.00	1.1328	26.56	22 04	28.25	1 2420	48.40	38 46
17.25	1.1350	27.00	22 38	28.50	1.2446	48.92	38.85
17.50	1.1373	27.46	22.74	28.75	1 2473	49 46	39.25
17.75	1.1395	27.90	23.08	29.00	1.2500	50.00	39 66
18.00	1.1417	28.34	23 42	29.25	1.2527	50.54	40.06
18.25	1.1440	28.80	23.77	29.50	1.2554	51.08	40.47
18.50	1.1462	29.24	24.11	29.75	1.2582	51.64	40.89
18.75	1.1485	29.70	24.47	30.00	1.2609	52.18	41 30
19.00	1.1508	30.16	24.82	30.25	1.2637	52 74	41 72
19.25	1.1531	30.62	25.18	30.50	1.2664	53 28	42 14
19.50	1.1554	31.08	25.53	30.75	1.2692	53.84	42 58
19.75	1.1577	31.54	25 88	31 00	1.2719	54.38	43 00
20.00	1.1600	32 00	26.24	31.25	1.2747	54.94	43.44
20.25	1.1624	32.48	26.61	31.50	1.2775	55.50	43 89
20.50	1.1647	32.94	26.96	31 75	1.2804	56 08	44 34
20.75	1.1671	33.42	27.33	32.00	1 2832	56.64	44.78
21.00	1.1694	33.88	27.67	32.25	1.2861	57.22	45.24

NITRIC ACID (Continued)

Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.	Degrees Baumé.	Sp. Gr. 60° / 60° F.	Degrees Twaddell.	Per Cent HNO_3.
32.50	1.2889	57.78	45.68	40.75	1.3909	78.18	63.48
32.75	1.2918	58.36	46.14	41.00	1.3942	78.84	64.20
33.00	1.2946	58.92	46.58	41.25	1.3976	79.52	64.93
33.25	1.2975	59.50	47.04	41.50	1.4010	80.20	65.67
33.50	1.3004	60.08	47.49	41.75	1.4044	80.88	66.42
33.75	1.3034	60.68	47.95	42.00	1.4078	81.56	67.18
34.00	1.3063	61.26	48.42	42.25	1.4112	82.24	67.95
34.25	1.3093	61.86	48.90	42.50	1.4146	82.92	68.73
34.50	1.3122	62.44	49.35	42.75	1.4181	83.62	69.52
34.75	1.3152	63.04	49.83	43.00	1.4216	84.32	70.33
35.00	1.3182	63.64	50.32	43.25	1.4251	85.02	71.15
35.25	1.3212	64.24	50.81	43.50	1.4286	85.72	71.98
35.50	1.3242	64.84	51.30	43.75	1.4321	86.42	72.82
35.75	1.3273	65.46	51.80	44.00	1.4356	87.12	73.67
36.00	1.3303	66.06	52.30	44.25	1.4392	87.84	74.53
36.25	1.3334	66.68	52.81	44.50	1.4428	88.56	75.40
36.50	1.3364	67.28	53.32	44.75	1.4464	89.28	76.28
36.75	1.3395	67.90	53.84	45.00	1.4500	90.00	77.17
37.00	1.3426	68.52	54.36	45.25	1.4536	90.72	78.07
37.25	1.3457	69.14	54.89	45.50	1.4573	91.46	79.03
37.50	1.3488	69.76	55.43	45.75	1.4610	92.20	80.04
37.75	1.3520	70.40	55.97	46.00	1.4646	92.92	81.08
38.00	1.3551	71.02	56.52	46.25	1.4684	93.68	82.18
38.25	1.3583	71.66	57.08	46.50	1.4721	94.42	83.33
38.50	1.3615	72.30	57.65	46.75	1.4758	95.16	84.48
38.75	1.3647	72.94	58.23	47.00	1.4796	95.92	85.70
39.00	1.3679	73.58	58.82	47.25	1.4834	96.68	86.98
39.25	1.3712	74.24	59.43	47.50	1.4872	97.44	88.32
39.50	1.3744	74.88	60.06	47.75	1.4910	98.20	89 76
39.75	1.3777	75.54	60.71	48.00	1.4948	98.96	91.35
40.00	1.3810	76.20	61.38	48.25	1.4987	99.74	93.13
40.25	1.3843	76.86	62.07	48.50	1.5026	100.52	95.11
40.50	1.3876	77.52	62.77				

Specific Gravity determinations were made at 60° F., compared with water at 60° F.

From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \frac{145}{\text{Sp. Gr.}}.$$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

ALLOWANCE FOR TEMPERATURE:

At 10° — 20° Bé. — 1/30° Bé. or .00029 Sp. Gr. = 1° F.
20° — 30° Bé. — 1/23° Bé. or .00044 " " = 1° F.
30° — 40° Bé. — 1/20° Bé. or .00060 " " = 1° F.
40° — 48.5° Bé. — 1/17° Bé. or .00084 " " = 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
HENRY HOWARD, ARTHUR WYMAN,
A. G. ROSENGARTEN, *Executive Committee*

New York, May 14, 1903.

NITRIC ACID

Lunge and Rey

Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams	
	% N_2O_5	% HNO_3	N_2O_5	HNO_3		% N_2O_5	% HNO_3	N_2O_5	HNO_3
1.000	0.08	0.10	1	1	1.195	27.10	31.62	324	378
1.005	0.85	1.00	8	10	1.200	27.74	32.36	333	388
1.010	1.62	1.90	16	19	1.205	28.36	33.09	342	399
1.015	2.39	2.80	24	28	1.210	28.99	33.82	351	409
1.020	3.17	3.70	33	38	1.215	29.61	34.55	360	420
1.025	3.94	4.60	40	47	1.220	30.24	35.28	369	430
1.030	4.71	5.50	49	57	1.225	30.88	36.03	378	441
1.035	5.47	6.38	57	66	1.230	31.53	36.78	387	452
1.040	6.22	7.26	64	75	1.235	32.17	37.53	397	463
1.045	6.97	8.13	73	85	1.240	32.82	38.29	407	475
1.050	7.71	8.99	81	94	1.245	33.47	39.05	417	486
1.055	8.43	9.84	89	104	1.250	34.13	39.82	427	498
1.060	9.15	10.68	97	113	1.255	34.78	40.58	437	509
1.065	9.87	11.51	105	123	1.260	35.44	41.34	447	521
1.070	10.57	12.33	113	132	1.265	36.09	42.10	457	533
1.075	11.27	13.15	121	141	1.270	36.75	42.87	467	544
1.080	11.96	13.95	129	151	1.275	37.41	43.64	477	556
1.085	12.64	14.74	137	160	1.280	38.07	44.41	487	568
1.090	13.31	15.53	145	169	1.285	38.73	45.18	498	581
1.095	13.99	16.32	153	179	1.290	39.39	45.95	508	593
1.100	14.67	17.11	161	188	1.295	40.05	46.72	519	605
1.105	15.34	17.89	170	198	1.300	40.71	47.49	529	617
1.110	16.00	18.67	177	207	1.305	41.37	48.26	540	630
1.115	16.67	19.45	186	217	1.310	42.06	49.07	551	643
1.120	17.34	20.23	195	227	1.315	42.76	49.89	562	656
1.125	18.00	21.00	202	236	1.320	43.47	50.71	573	669
1.130	18.66	21.77	211	246	1.325	44.17	51.53	585	683
1.135	19.32	22.54	219	256	1.330	44.89	52.37	597	697
1.140	19.98	23.31	228	266	1.3325	45.26	52.80	603	704
1.145	20.64	24.08	237	276	1.335	45.62	53.22	609	710
1.150	21.29	24.84	245	286	1.340	46.35	54.07	621	725
1.155	21.94	25.60	254	296	1.345	47.08	54.93	633	739
1.160	22.60	26.36	262	306	1.350	47.82	55.79	645	753
1.165	23.25	27.12	271	316	1.355	48.57	56.66	658	768
1.170	23.90	27.88	279	326	1.360	49.35	57.57	671	783
1.175	24.54	28.63	288	336	1.365	50.13	58.48	684	798
1.180	25.18	29.38	297	347	1.370	50.91	59.39	698	814
1.185	25.83	30.13	306	357	1.375	51.69	60.30	711	829
1.190	26.47	30.88	315	367	1.380	52.52	61.27	725	846

NITRIC ACID (Continued)

Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams	
	% N_2O_5	% HNO_3	N_2O_5	HNO_3		% N_2O_5	% HNO_3	N_2O_5	HNO_3
1.3833	53.08	61.92	735	857	1.495	78.52	91.60	1174	1369
1.385	53.35	62.24	739	862	1.500	80.65	94.09	1210	1411
1.390	54.20	63.23	753	879	1.501	81.09	94.60	1217	1420
1.395	55.07	64.25	768	896	1.502	81.50	95.08	1224	1428
1.400	55.97	65.30	783	914	1.503	81.91	95.55	1231	1436
1.405	56.92	66.40	800	933	1.504	82.20	96.00	1238	1444
1.410	57.86	67.50	816	952	1.505	82.63	96.39	1244	1451
1.415	58.83	68.63	832	971	1.506	82.94	96.76	1249	1457
1.420	59.83	69.80	849	991	1.507	83.26	97.13	1255	1464
1.425	60.84	70.98	867	1011	1.508	83.58	97.50	1260	1470
1.430	61.86	72.17	885	1032	1.509	83.87	97.84	1265	1476
1.435	62.91	73.39	903	1053	1.510	84.09	98.10	1270	1481
1.440	64.01	74.68	921	1075	1.511	84.28	98.32	1274	1486
1.445	65.13	75.98	941	1098	1.512	84.46	98.53	1277	1490
1.450	66.24	77.23	961	1121	1.513	84.63	98.73	1280	1494
1.455	67.38	78.60	981	1144	1.514	84.78	98.90	1283	1497
1.460	68.56	79.98	1001	1168	1.515	84.92	99.07	1287	1501
1.465	69.79	81.42	1023	1193	1.516	85.04	99.21	1289	1504
1.470	71.06	82.90	1045	1219	1.517	85.15	99.34	1292	1507
1.475	72.39	84.45	1068	1246	1.518	85.26	99.46	1294	1510
1.480	73.76	86.05	1092	1274	1.519	85.35	99.57	1296	1512
1.485	75.18	87.70	1116	1302	1.520	85.44	99.67	1299	1515
1.490	76.80	89.60	1144	1335					

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID AND ITS SALTS (METHOD OF SMITH)

In titrating free phosphoric acid it must be borne in mind that NaH_2PO_4 reacts acid to phenolphthalein and neutral to methyl orange, while Na_2HPO_4 is neutral to phenolphthalein and basic to methyl orange. The reactions are shown as follows:

$H_3PO_4 + 2NaOH = 2H_2O + Na_2HPO_4$ (neutral to P. acid to M.O.).
$H_3PO_4 = NaOH = NaH_2PO_4 = H_2O + NaH_2PO_4$ (neutral to M.O. acid to P).

J. H. Smith outlines the following process for analysis of phosphoric acid free and combined:

Procedure.—Take five or six grams of the material and dissolve in the minimum quantity of distilled water. Add two drops of phenolphthalein. If the solution is not colored pink by the indicator the absence of trisodium phosphate (Na_3PO_4) and sodium carbonate (Na_2CO_3) may be assumed. Heat to 55° C. and titrate with N/1 NaOH to the characteristic pink end-point, being particularly careful to keep the temperature at 55° C. when near the end-point. This precaution should be observed in all the titrations as the temperature governs the accuracy of the titrations (see paper by Smith).

Record this titration as " *A* " and the ml. NaOH required as (*a*).

The solution is now titrated back with N/1 HCl, using a few drops of methyl orange as indicator, to the pink end-point.

Record this titration as " *B* " and the ml. acid required as (*b*).

Calculation of the Composition.—If the solution contains only $Na_2HPO_4 + NaH_2PO_4$ or $NaH_2PO_4 + H_3PO_4$ or only one of these compounds we may assume the following:

If (*a*) is greater than (*b*)

$$(a) - (b) = \text{ml. equivalent of N/1 } H_3PO_4,$$
$$(b) = \text{ml. equivalent of N/1 } NaH_2PO_4.$$

If (*b*) is greater than (*a*)

$$(b) - (a) = Na_2HPO_4,$$
$$(a) = NaH_2PO_4.$$

If $(a) = (b)$

$$\text{Each titration} = NaH_2PO_4 \text{ present.}$$

If $(a) = 2(b)$

$$\text{Only } H_3PO_4 \text{ is present.}$$

To Ascertain the Presence of Other Salts.—Add N/1 HCl (ml. HCl the same as ml. in titration *B*). Call this (*b'*). Boil for at least 15 minutes. By this procedure metaphosphoric acid or its salts is converted to the orthophosphate form, alkaline salts containing carbonates are destroyed and CO_2 evolved. Cool the solution to 55° C. and titrate back with N/1 NaOH first to " *B* " point in which (*b''*) ml. of alkali is used, and finally to third end-point (*C*), where the phenolphthalein pink color is reached. The ml. N/1 NaOH required is recorded as (*c*).

In titrating back after boiling, the (b'') amount of alkali required to reach the methyl orange point where the pink coloration just appears should always be the same amount as the (b') excess of acid added for boiling (except in the case of polyphosphates being present—see paper). A slight loss of HCl during boiling may cause (b'') to be less than (b'). In any case it is preferable to consider the point reached after addition of the (b'') quantity of alkali as the identical point with B, so that (b') and (b'') are not used in the calculation, but simply employed as a comparative check on each other.

If the " C " point coincides with the " A " point, i.e., if $(c) = (b)$ metaphosphoric acid and its salts as well as carbonates in the original substances are excluded.

If (c) is greater than (b) the presence of metaphosphates is indicated.

If (c) is less than (b) carbonates are evidently present.

With the aid of the three fixed points " A," " B," " C " and the amounts of acid or alkali required to reach them, i.e., (a), (b) and (c) it is possible to calculate the percentages of practically all the phosphoric acids and their salts, which may exist together in a compound, including the carbonates and the free alkali. which may be present with them.

CALCULATION OF CONSTITUENTS IN A MIXTURE OF PHOSPHATES

If (a) is greater than (b)

$(a)-(b)=H_3PO_4$, $2(b)-(a)=NaH_2PO_4$, $(c)-(b)=NaPO_3$ (generally nil).

If (a) is greater than $2(b)$

Then $(a)-2(b)=$ measure of metaphosphoric acid or the foreign acid present.

If (a) is less than (b)

(a) is the measure of NaH_2PO_4, $(b)-(a)=Na_2HPO_4$,

$(c)-(b)=NaPO_3$ (usually nil).

With alkaline salts " C " coincides with "A," i.e., when no carbonate is present.

If (a) is less than (b) then

(a) is a measure of Na_3PO_4, $(b)-(a)=Na_2HPO_4$.

Where (c) is less than (b), i.e., when carbonate is present.

If (a) is less than (b)

$(a)+(c)-(b)=Na_3PO_4$, $(b)-(a)=Na_2HPO_4$, $(b)-(c)=Na_2CO_3$.

Where no carbonate is present and (a) is greater than (b).

$(b)=Na_3PO_4$, $\frac{1}{2}(a-b)=Na_2O$.

Where carbonate is present and (a) is greater than (b)

$(b)-(c)=Na_2CO_3$, $(c)=Na_3PO_4$, $\frac{1}{2}(a-b)=Na_2O$.

In calculating the weight of constituents from the above formulae, since normal solutions are used in the titrations each ml. is equivalent to molecular weights divided by 1/1000. In case of Na_2CO_3 and Na_2O the absolute weights are 1/2000 of the respective molecular weights.

[14] J. H. Smith, Soc. Chem. Ind., **36**, 415 (1917).

Formulae	Mol. Wt.	1 ml. Equivalent of Titration	Formulae	Mol. Wt.	1 ml. Equivalent of Titration
H_3PO_4	98.14	0.09814 g.	$NaPO_3$	80.05	0.08005 g.
NaH_2PO_4	120.05	0.12005	Na_2CO_3	106.01	0.053005
Na_2HPO_4	142.05	0.14205	Na_2O	62.00	0.031
Na_3PO_4	164.04	0.16404			

With water of crystallization $NaH_2PO_4 \cdot H_2O = 138.07$, $NaH_2PO_4 \cdot 2H_2O = 156.09$, $Na_2HPO_4 \cdot 12H_2O = 358.24$, $Na_3PO_4 \cdot 12H_2O = 380.23$, $Na_2CO_3 \cdot 10H_2O = 286.17$, $Na_2CO_3 \cdot H_2O = 124.02$.

Notes.—In presence of meta or pyro acids and their salts it is well to verify the results with qualitative tests. When pyro acid is present point "*A*" is obscured and lies much nearer "B," but the correct "*A*" point is "*C*" obtained after boiling with the excess acid.

In presence of metaphosphate it is advisable to repeat titrations employing N/1 H_2SO_4 and evaporating to near dryness to completely convert the meta to ortho compound.

Phosphates attack glass combining with the alkali present. The presence of NaCl obtained in the titrations counteracts this action.

PHOSPHORIC ACID AT 17.5°

Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.	Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.	Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	33 06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15.84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

ANALYSIS OF SULFURIC ACID

Sulfuric acid made by the contact process is exceedingly pure, the principal impurity being iron, which causes turbidity in strong acid. The acid made by this process is 99% strength. This is diluted to 66° Bé (93.19% H_2SO_4) and is known as oil of vitriol. The acid is also commonly marketed as 60° Bé acid (77.67% H_2SO_4) and 50° Bé acid (62.18% H_2SO_4) obtained by further dilution of the stronger acid. 50° Bé acid is also obtained by the chamber process; this acid is not as pure as that produced by the contact process. The impurities occurring in sulfuric acid are iron, lead, copper, zinc, antimony, selenium, arsenic, sulfur dioxide, hydrochloric acid, hydrofluoric acid, nitric acid.

Sulfuric acid up to 93% strength may be determined with a fair degree of accuracy by ascertaining its specific gravity by means of a hydrometer and referring to the tables on sulfuric acid.

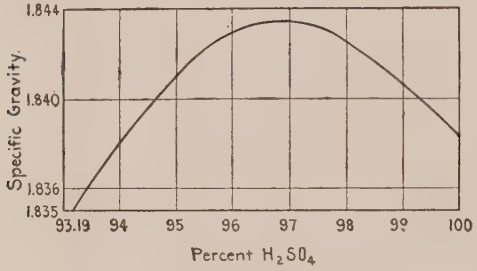

Fig. 306.

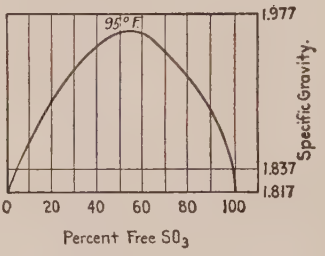

Fig. 307.

Specific Gravity Charts—Sulfuric Acid.

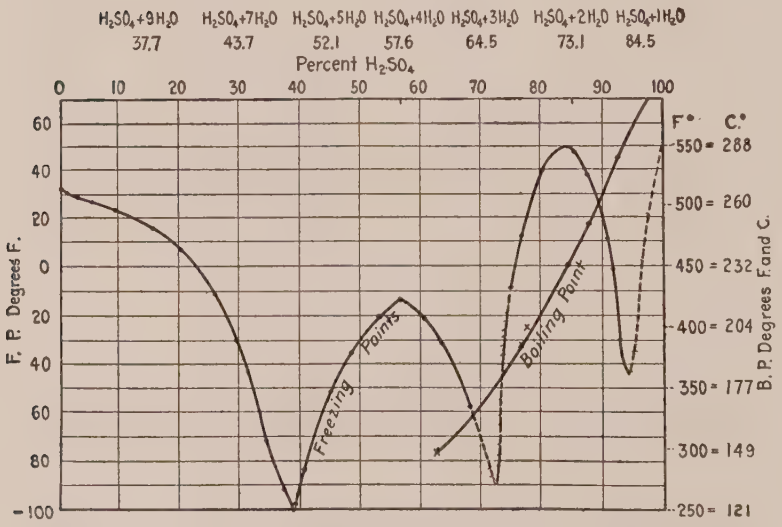

Fig. 308. Chart Showing Freezing- and Boiling-points of Sulfuric Acid of Varying Concentration.

Sulfuric acid readily absorbs SO_3 so that its acidity may be considerably over 100%. This acid, commonly known as oleum, fumes when exposed to the air due to its low vapor tension, the SO_3 combining with the moisture of the air with formation of H_2SO_4 mist.

SULFURIC ACID

METHOD OF ANALYSIS [15]

Procedure for Titration with Standard NaOH.—Concentrated sulfuric acid absorbs moisture rapidly so that the weighing should be made quickly, the acid having been placed in a special closed receptacle as recommended on pages 2200 to 2203. Such an amount of acid is taken as will require a titration that can be read on the chamber burette used. For example if normal caustic is used and the chamber burette reads from 75 ml. to 100 ml. the acid should contain from 3.7 grams to 4.9 grams of H_2SO_4. The acid is added to CO_2 free distilled water, preferably in a porcelain casserole, 1 ml. of 1% phenolphthalein added and the titration made to a faint pink color with standard NaOH. It is advisable to titrate the acid using methyl orange if the presence of CO_2 is suspected in the water. Some chemists prefer the use of this indicator. It is a common practice to standardize the acidimetric and alkalimetric reagents in presence of methyl orange and phenolphthalein in separate titrations, recording factors for each.

The temperature of the titrating alkali should be noted and a correction of 0.032 ml. be made for each degree deviation from the temperature at which the reagent was standardized. For each 1° C. that the temperature is above that at standardization subtract this correction, and add this for each degree the temperature is below that at standardization.

(ml. titration $\times$ H_2SO_4 value per ml. $\times$ 100) $\div$ wt. of sample = % H_2SO_4.

DETERMINATION OF IMPURITIES IN SULFURIC ACID

Determination of Residue on Heating

50 to 100 grams of the acid are weighed into a platinum or silica dish and the acid evaporated (Hood) by heating gently over a direct flame. When no more fumes evolve, the dish is cooled and weighed. The increased weight of the dish is due to the residue, composed of substances not volatile at red heat and generally contains iron oxide. Chamber acid may have all of the substances occurring in sulfur ores present in this residue.

[15] Certain details of procedure are published by courtesy of the General Chemical Company.

Determination of Lead

Minute Amounts.—Determine by means of the colorimeter according to the procedure described on page 517, Vol. I.

High Lead Contamination.—Larger amounts of lead sulfate may be determined gravimetrically. The lead may be extracted from the residue, obtained on evaporation of the acid and heating, by extracting with ammonium acetate according to the standard procedure, and lead precipitated from the extract made acid with acetic by addition of a small excess of $K_2Cr_2O_7$ solution.

If preferred, lead may be determined as follows: 100 grams of the acid are diluted with an equal volume of distilled water and the solution stirred and cooled. Twice the volume of alcohol is added, the lead sulfate allowed to settle for two hours or more and the precipitate filtered on a Gooch crucible, the residue washed with alcohol, dried and ignited at dull red heat and weighed as $PbSO_4$. If contamination of the lead sulfate is suspected, this residue may be extracted with ammonium acetate and lead precipitated from the extract as $PbCrO_4$ according to the regular procedure.

$$PbCrO_4 \times .641 = Pb. \qquad PbSO_4 \times .6331 = Pb.$$

Determination of Iron

Traces of Iron.—The colorimetric procedure is used, iron being determined by color comparison of the thiocyanate with standards. See procedure on page 486, Vol. I. Five grams of the acid are added to 10 ml. of water in a small beaker and the solution heated to dissolve any iron in suspension. The cooled acid is poured into a 100 ml. Nessler tube with rinsing of the beaker. A few drops of N/10 $KMnO_4$ are added in amount sufficient to obtain a faint pink color, then 10 ml. of a 10% solution of NH_4CNS and the solution made up to 100 ml. Comparison is now made as follows:

The standard is prepared by treating 5 ml. of iron-free sulfuric acid in exactly the same manner as the tested sample, in a separate Nessler tube. Standard iron solution is run in, stirring the solution with a glass plunger, until the color matches that of the sample. It is advisable to make the standard solution to contain 0.00005 g. Fe per 1 ml. Then each ml. will represent 0.001% Fe.

High Iron.—If 0.02% of iron or over is present dilute 25 to 50 grams of the acid with distilled water. Add a few crystals of $KClO_3$ and boil. Cool and add a slight excess of NH_4OH. When the iron hydroxide has settled, filter and wash with hot water. Dissolve the precipitate with HCl (1 : 1) catching the solution in a casserole. Wash the iron out of the paper. Heat the combined filtrate to boiling and titrate with standard $SnCl_2$ solution. See page 484, Vol. I.

If antimony or arsenic is present the solution turns dark during the titration. If this occurs treat a fresh sample, diluted, with H_2S to remove As and Sb, and determine iron in the filtrate from the sulfides.

Determination of Arsenic

Traces of Arsenic. Amounts less than .00005%.—Take 50 grams or more of the acid and distill off the arsenic as $AsCl_3$ according to the distillation

method given on page 91. Determine arsenic in the distillate by the Gutzeit method.

Amounts less than .005% may be determined directly by the Gutzeit method. When the arsenic is greater than 0.05% it may be determined by reducing the arsenic with tartaric acid and titrating with standard iodine solution, after neutralizing the acid with ammonia and adding sodium bicarbonate. 25–50 grams of the acid are taken and placed in a Kjeldahl flask and $\frac{1}{2}$ gram of tartaric acid added together with 2 grams of fused potassium bisulfate. The acid is heated over the direct flame until the color, first becoming dark, changes to a straw color. Fuming will cause loss of arsenic and should be avoided. The acid is washed into a beaker with 250 ml. of water, then neutralized with NH_4OH, and $NaHCO_3$ added. The titration with iodine is made in presence of starch. The end-point is a blue color.

If antimony is present a separation of the arsenic must be made by distillation. 1 ml. N/10 I = .003748 g. As or .004948 g. As_2O_3. $As_2O_3 \times 1.11616 = As_2O_5$.

Determination of Antimony

The arsenic is first removed by distillation as $AsCl_3$ (page 91, Vol. I). The antimony is now distilled by adding 20 grams of zinc dissolved in 20 grams of concentrated HCl. The antimony in the distillate is determined by the modified Gutzeit method given in the chapter on Antimony, Vol. I.

Determination of Zinc

25 to 50 ml. of the acid are evaporated to dryness in a silica dish. The residue is treated with a strong solution of NH_4Cl and NH_4OH solution. After filtering off the ferric hydroxide, the filtrate containing the zinc is neutralized with H_2SO_4 and 10 ml. added in excess (sp.gr. $H_2SO_4 = 1.84$). Potassium ferrocyanide is now added in such amount that the solution will contain about 2.5%. Compare the turbidity with standards.

With larger amounts of zinc the zinc is determined by titrating with standard potassium ferrocyanide. See chapter on Zinc, Vol. I.

The zinc may be determined gravimetrically on a 200-gram sample. The acid is fumed off until only 2–5 ml. remains in the dish. Water is added, the solution neutralized with ammonia, sufficient dilute H_2SO_4 added to make a 2.5% free acid. Copper, lead, etc., are removed as sulfides by gassing with H_2S. Zinc is determined in the filtrate, after oxidation of the iron with bromine and removing it by adding NH_4OH and NH_4Cl. Zinc is precipitated as ZnS from the filtrate made acid (2% free acid) with formic acid, by H_2S. The washed sulfide is ignited and weighed as ZnO. $ZnO \times .8034 = Zn$.

Copper.—This is determined colorimetrically. 25–50 ml. of the acid are evaporated to dryness, the residue taken up with 100 ml. of water, 2 ml. HCl (sp.gr. 1.19) added and copper precipitated with H_2S. The washed precipitate is dissolved in HNO_3 and the solution made ammoniacal with ammonia. The color is now matched with standards containing known amounts of copper.

Determination of Selenium

Traces.—10 ml. of the acid diluted with an equal volume of water are placed in a test tube and 4 or 5 drops of 1% KI solution added. Heat to boiling to expel free iodine. The brick red color is compared with standards containing known amounts of selenium made up in the same way as the sample. If sufficient selenium in present this is thrown down as a brick red finely divided precipitate.

Standard selenium solution is prepared by dissolving .1 g. pure Se in 5 ml. HNO_3 and 10 ml. HCl. The solution is evaporated to dryness, then taken up with water and a little dilute H_2SO_4 and made up to 1000 ml. 1 ml.=.0001 g. Se.

Larger Amounts.—500 grams of the acid is diluted by pouring into a liter of water, 100 ml. concentrated HCl added and the solution saturated with SO_2. The selenium is allowed to settle 15 to 20 hours, then filtered through a filter of fine texture. The precipitate is dissolved by placing the filter and precipitate in sulfuric acid nitric acid mixture 5 ml. H_2SO_4+50 ml. HNO_3. The solution is evaporated to fumes, adding more HNO_3 if the solution is dark, and again evaporated to expel HNO_3. After diluting with water and filtering, the filtrate is made up to about 100 ml. and gassed boiling hot with H_2S. The precipitated selenium is settled, filtered into a Gooch, washed with water, then alcohol and ether and dried with a current of warm air to constant weight.

Sulfur Dioxide Determination in Sulfuric Acid.—1–10 ml. of N/10 iodine solution are run into 200 ml. of water, starch solution is added and the acid to be tested is allowed to flow from a burette into this reagent, until the blue color disappears.

1 ml. N/10 iodine = .0032 g. SO_2.

SULFURIC ACID

Hydrochloric Acid Determination in Sulfuric Acid.—50 to 100 ml. of the acid is diluted to about 200 ml. by running the acid into chlorine-free water 10 ml. of 1% silver nitrate solution is added and the turbidity compared against a standard made by adding standard sodium chloride solution from a burette into a solution containing an equal amount of sulfuric acid (free from chloride) diluted with water and containing silver nitrate as in case of the sample. When the turbidity is the same as the sample the number of ml. of NaCl solution is noted. The turbidity is best seen by placing the two solutions side by side on a black paper. Standard chloride solution contains .16 g. NaCl per liter. 1 ml. = .0001 g. HCl.

If considerable hydrochloric acid is present it may be determined by Volhard's method given on page 271, Vol. I. The sample of acid is diluted to about 20% strength. A measured excess of N/10 $AgNO_3$ added and the excess titrated with N/10 NH_4CNS solution in presence of ferric ammonium alum.

1 ml. N/10 $AgNO_3$ = .003647 g. HCl.

Determination of Nitric Acid

Traces.—In absence of selenium traces of HNO_3 may be determined colorimetrically. To 100 ml. of the acid $\frac{1}{2}$ ml. saturated solution of $FeSO_4$ is

added. Comparison is made in a Nessler tube with a standard by adding to 100 ml. H_2SO_4, $\frac{1}{2}$ ml. $FeSO_4$ solution and running in standard HNO_3 until the color matches, the solution being stirred with a plunger during the addition. Standard HNO_3 solution should contain .0001 g. HNO_3 per ml.

Larger Amounts.—See method on page 2216.

Determination of Fluorine.—This is determined by the etch test described in Vol. I, page 421. The acid should not contain over 10% H_2O. Strengthen with oleum if necessary.

THE ANALYSES OF OLEUM OR FUMING SULFURIC ACID AND OF MIXED ACID

The analyses of fuming sulfuric acid and mixed acid are placed under one general scheme as the procedure for oleum is included in that of mixed acid. The term oleum is given to concentrated sulfuric acid containing free SO_3,

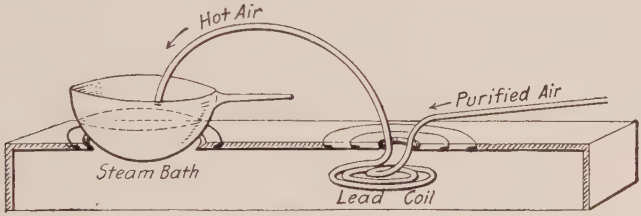

FIG. 309. Method for Rapid Evaporation of Liquids.

the combined water in the product decreasing (along with sulfuric acid) with the increase of free SO_3 or sulfuric anhydride. Mixed acid is the technical name for the mixture of concentrated sulfuric acid and nitric acid or of oleum and nitric anhydride, the product being commonly used in nitrating glycerine, cotton and other materials. The analysis includes the determinations of H_2SO_4, HNO_3, N_2O_5, N_2O_3 and in the case of oleum, the determination of SO_3. In the presence of the latter, HNO_3 is assumed to lose its combined water according to the reaction:

$$2HNO_3+SO_3=H_2SO_4+N_2O_5.$$

In absence of nitric acid SO_2 may be present. It is assumed that if HNO_3 is present the SO_2 is oxidized to SO_3 with formation of H_2SO_4 and the anhydrides SO_3 and N_2O_3 according to the reaction.

$$N_2O_5+H_2O+2SO_2=N_2O_3+SO_3+H_2SO_4.$$

Some chemists prefer to express the reaction:

$$2HNO_3+SO_2=H_2SO_4+N_2O_4.$$

The analysis is carried out by three titrations—(*a*) determination of total acidity, (*b*) determination of sulfuric acid including SO_3 free in case of oleum, (*c*) determination of lower oxides.

For economy of time the following order should be observed: The sample for the determination of sulfuric acid and free SO_3 (oleum) should be weighed, diluted with water according to the detailed procedure and placed on the steam bath for evaporation. During the evaporation the titration for total acidity of the sample and the titration for the lower oxides are made and finally that of oleum on the evaporated sample.

Special Reagents: ***Normal Sodium Hydroxide.***—One ml. = 0.04904 gram H_2SO_4.

Tenth Normal Potassium Permanganate.—3.16 grams $KMnO_4$ per liter. Standardized against N/10 solution of Sorensen's Sodium Oxalate. (See Preparation of Standard Reagents.) One ml. = 0.0019 gram N_2O_3, or 0.002351 gram HNO_2.

PROCEDURE. TOTAL ACIDS

The sample is accurately weighed by one of the procedures recommended for strong acids. The Dely or Blay-Burkhard tubes are best for this purpose. Such a weight being taken as will require a titration between 75 and 100 ml., e.g., containing an equivalent of 3.675 grams to 4.9 grams H_2SO_4. The acid is now run under cold CO_2 free water according to directions on pages 2201 and 2202, and the acid titrated with N/1 solution of NaOH.

One ml. NaOH = 0.04904 g. H_2SO_4. Calculate to $\% \frac{\text{ml. NaOH} \times .04904 \times 100.}{\text{Weight of acid taken}}$

LOWER OXIDES

Ten ml. of the sample, weighed in a pipette with capillary delivery tip, are cautiously run into about 400 ml. of cold water, keeping the delivery tip well under the water and in rapid motion to prevent overheating through local action. The mixture is titrated with N/10 $KMnO_4$ until a pink tint is obtained that does not fade in three minutes.

1 ml. N/10 $KMnO_4$ = 0.0019 g. N_2O_3 (N_2O_3 to N_2O_4 factor = 2.42.)
1 ml. N/10 $KMnO_4$ = 0.0046 g. N_2O_4.
1 ml. N/10 $KMnO_4$ = 0.00235 g. HNO_2. Equivalent H_2SO_4 = 0.0049043 g. per ml.
1 ml. N/10 $KMnO_4$ = 0.0032035 g. SO_2.
1 ml. N/10 $KMnO_4$ = 0.0041043 g. H_2SO_3.

Note.—With exactly N/10 $KMnO_4$ on a 19-gram sample 1 ml. = 0.01% N_2O_3.

SULFURIC ACID AND FREE SO_3

The sample is weighed in a Dely tube and run under cold water, as in case of total acids, using in this case about 45 to 50 ml. of water in a 4-in. casserole. The solution is evaporated on the steam bath to expel the volatile acids, lower

oxides and nitric. The evaporation is hastened by blowing a current of hot, dry, pure air over the sample, see Fig. 309. Instead of a casserole, a shallow glass cell, 3 inches in diameter and $1\frac{1}{2}$ inches deep may be used. The air current in this case is unnecessary. About 5 ml. of water are added and this again evaporated off. The acid thus obtained is $H_2SO_4+SO_3$.

The acid is taken up with water and titrated with standard caustic, using CO_2 free water and phenolphthalein indicator.

One ml. N/1 NaOH = 0.004904 gram H_2SO_4.

NITRIC ACID

This may be obtained from the above determinations according to calculations following. It may be obtained by direct titration with standard ferrous sulfate, by running a weighed amount of mixed acid into 100 ml. of cold sulfuric acid and titrating to a yellowish red tint. For the detailed procedure see Nitric Acid, page 2216.

Calculation of Results. ***A. Nitric Acid and SO_2 being Absent.***—The total acidity is calculated to SO_3. Reference is made to the table for Oleum from which the % H_2SO_4 and free SO_3 are obtained.

Example.—Suppose the total acidity in terms of SO_3 was found to be 84.2. The acid contains 86% H_2SO_4 and 14% free SO_3.

B. Nitric Acid Absent, SO_2 is Present in the Mixture. **Total SO_3.**—From total acidity as SO_3 subtract $SO_2 \times 1.25$ (i.e., equivalent SO_3).

Combined Water.—100 − (total SO_3+SO_2) = H_2O.

Combined SO_3.—$H_2O \times 4.4445 = SO_3$ equivalent or combined SO_3.

Free SO_3.—Total SO_3 − combined SO_3 = free SO_3.

Sulfuric Acid.—Combined SO_3+H_2O.

Example.—If SO_2 was found to be 2% and the total acidity in terms of SO_3 = 83.5%.

Total $SO_3 = 83.5 - (2 \times 1.25) = 81\%$.

Water = 100 − (81 + 2) = 17%. *Report*

Combined $SO_3 = 17 \times 4.4445 = 75.56\%$ Sulfuric acid = 92.56%.

Free $SO_3 = 81 - 75.56 = 5.44\%$. Free $SO_3 = 5.44$.

Sulfuric acid = 75.56 + 17 = 92.56%. $SO_2 = 2.00$. Total 100.

C. Nitric Acid Present and SO_2 Absent.—Nitric acid in presence of free SO_3 is assumed to be the anhydride N_2O_5.

N_2O_5.—From the total acidity is subtracted the acidity after evaporation, both being calculated to equivalent SO_3. The difference multiplied by 1.349 = % N_2O_5.

H_2O.—Total SO_3 (after evaporation) + N_2O_5 subtracted from 100 = H_2O.

Combined SO_3.—$H_2O \times 4.4445 = SO_3$ equivalent to H_2O.

Free SO_3.—Combined SO_3 subtracted from total SO_3 = free SO_3.

Sulfuric Acid.—Combined $SO_3+H_2O = H_2SO_4$.

Example.—If total acidity = 84% in terms of SO_3 and the total SO_3 (after evaporation) = 82%, then the difference $2 \times 1.349 = 2.698\%$ N_2O_5.

Water = 100 − (82 + 2.698) = 15.302%. *Report*

Combined $SO_3 = 15.302 \times 4.4445 = 68.01\%$.
Free $SO_3 = 82 - 68.01 = 13.99\%$.
$H_2SO_4 = 68.01 + 15.302 = 83.312\%$.

$H_2SO_4 = 83.312\%$.
Free $SO_3 = 13.980\%$.
$N_2O_5 = 2.698\%$.
Total 100.

D. N_2O_5 Required to be Reported as HNO_3, 96%.[16]—***HNO_3, 96%*** = SO_3 equivalent (acid expelled by evaporation) $\times 1.64$. $100 - \%$ HNO_3 (96%) = oleum. Total SO_3 in oleum $= \frac{100 \times \text{total } SO_3}{\text{per cent oleum}}$.

Reference to the oleum table will give the per cent free SO_3 in the oleum.

Example.—Suppose total acidity in terms of $SO_3 = 84\%$ and the SO_3 after evaporation = 82%, then HNO_3, 96% = the difference $= 2 \times 1.64 = 3.28\%$ HNO_3 (96%).

Oleum $= 100 - 3.28 = 96.72\%$.

Total SO_3 in oleum $= 100 \times 82$ divided by $96.72 = 84.78$.

From the oleum table 84.78 gives 17.10% free SO_3.

Report

Nitric acid, 96% =	3.28%
Oleum	= 96.72%
Free SO_3	= 17.10%
Total SO_3	= 84.78%

The nitric acid and oleum make a total of 100.

Formulae for Diluting or Strengthening Solutions.—To dilute a solution with water:

(*a*) $\frac{DZ}{A} = X$; $\quad Y = Z - X$; $\quad$ or $\quad$ (*b*) $\frac{A - DX}{D} = Y$.

To dilute a strong with a weaker liquid:

(*a*) $\frac{A - DZ}{A - B} = Y$; $\quad X - Z = Y$; $\quad$ or $\quad$ (*b*) $\frac{A - DX}{D - B} = Y$.

To strengthen a weak with a stronger liquid:

(*a*) $\frac{D - AZ}{C - A} = X$; $\quad Y = Z - X$; $\quad$ or $\quad$ (*b*) $\frac{D - AY}{C - D} = X$.

A = actual concentration of the solution that is to be corrected;
B = concentration of the diluting solution;
C = concentration of the strengthening solution;
D = desired concentration;
X = amount of the stronger solution to be added, taken or prepared;
Y = amount of weaker solution to be added or taken;
Z = amount of solution desired or given.
All data are in terms of weight of the constituents.

[16] This is the usual strength of the commercial concentrated acid.

DILUTION OF SOLUTIONS

If a = per cent of solution desired, b = specific gravity of solution to be diluted and c its percentage then
Volume or ratio of the strong solution is d

$$\frac{a}{b \times \frac{1}{100} c} = d.$$

Volume or ratio of water required

$$100 - \frac{a}{c \div 100} \text{ or } 100 - b \times d.$$

Example.—To make 75% sulfuric acid from 87% solution having a specific gravity of 1.8.

Substituting in above formula $\frac{75}{1.8 \times 0.87}$ = ml. or liters or cubic feet, etc. of acid to be taken, i.e. ratio is 47.9 and $100 - \frac{75}{0.87}$ = ml. or liters or cubic feet of water required for dilution, i.e. ratio is 13.79.

47.9 ml. of the strong acid diluted with 13.79 ml. of water will make the acid 75% strength.

It is evident that the ratio being known large volumes of solution may be made so that the procedure is applicable for factory use.

SULFURIC ACID

By W. C. Ferguson and H. P. Talbot

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.*	Pounds O. V. in 1 Cubic Foot.
0	1.0000	0.0	0.00	62.37	0.00	0.00
1	1.0069	1.4	1.02	62.80	1.09	0.68
2	1.0140	2.8	2.08	63.24	2.23	1.41
3	1.0211	4.2	3.13	63.69	3.36	2.14
4	1.0284	5.7	4.21	64.14	4.52	2.90
5	1.0357	7.1	5.28	64.60	5.67	3.66
6	1.0432	8.6	6.37	65.06	6.84	4.45
7	1.0507	10.1	7.45	65.53	7.99	5.24
8	1.0584	11.7	8.55	66.01	9.17	6.06
9	1.0662	13.2	9.66	66.50	10.37	6.89
10	1.0741	14.8	10.77	66.99	11.56	7.74
11	1.0821	16.4	11.89	67.49	12.76	8.61
12	1.0902	18.0	13.01	68.00	13.96	9.49
13	1.0985	19.7	14.13	68.51	15.16	10.39
14	1.1069	21.4	15.25	69.04	16.36	11.30
15	1.1154	23.1	16.38	69.57	17.58	12.23
16	1.1240	24.8	17.53	70.10	18.81	13.19
17	1.1328	26.6	18.71	70.65	20.08	14.18
18	1.1417	28.3	19.89	71.21	21.34	15.20
19	1.1508	30.2	21.07	71.78	22.61	16.23
20	1.1600	32.0	22.25	72.35	23.87	17.27
21	1.1694	33.9	23.43	72.94	25.14	18.34
22	1.1789	35.8	24.61	73.53	26.41	19.42
23	1.1885	37.7	25.81	74.13	27.69	20.53
24	1.1983	39.7	27.03	74.74	29.00	21.68

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Sp. Grs., the corresponding degrees Baumé were calculated by the following formula: Baumé $= 145 - 145/\text{Sp. Gr.}$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

* 66° Baumé = Sp. Gr. 1.8354 = Oil of Vitriol (O. V.).

1 cu. ft. water at 60° F. weighs 62.37 lbs. av.

Atomic weights from F. W. Clarke's table of 1901. **O = 16.**

H_2SO_4 = 100 per cent.

	% H_2SO_4	% O. V.	%60°
O. V.	= 93.19	= 100.00	= 119.98
60°	= 77.67	= 83.35	= 100.00
50°	= 62.18	= 66.72	= 80.06

SULFURIC ACID (Continued)

Degrees Baumé.	*Freezing (Melting) Point. F.
0	32.0
1	31.2
2	30.5
3	29.8
4	28.9
5	28.1
6	27.2
7	26.3
8	25.1
9	24.0
10	22.8
11	21.5
12	20 0
13	18.3
14	16.6
15	14.7
16	12.6
17	10.2
18	7.7
19	4.8
20	+ 1.6
21	− 1.8
22	− 6.0
23	−11
24	−16

APPROXIMATE BOILING POINTS

50° B,	295° F.
60° "	386° "
61° "	400° "
62° "	415° "
63° "	432° "
64° "	451° "
65° "	485° "
66° "	538° "

FIXED POINTS

Specific Gravity.	Per Cent H_2SO_4.	Specific Gravity.	Per Cent H_2SO_4.
1.0000	.00	1.5281	62.34
1.0048	.71	1.5440	63.79
1.0347	5.14	1.5748	66.51
1.0649	9.48	1.6272	71.00
1.0992	14.22	1.6679	74.46
1.1353	19.04	1.7044	77.54
1.1736	23.94	1.7258	79.40
1.2105	28.55	1.7472	81.32
1.2513	33.49	1.7700	83.47
1.2951	38.64	1.7959	86.36
1.3441	44.15	1.8117	88.53
1.3947	49.52	1.8194	89.75
1.4307	53.17	1.8275	91.32
1.4667	56.68	1.8354	93.19
1.4822	58.14		

Acids stronger than 66° Bé. should have their percentage compositions determined by chemical analysis.

* Calculated from Pickering's results, Jour. of Lon. Ch. Soc., vol. 57, p. 363.

AUTHORITIES — W. C. FERGUSON; H. P. TALBOT.

This table has been approved and adopted as a standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER,
HENRY HOWARD,
JAS. L. MORGAN,
ARTHUR WYMAN,
A. G. ROSENGARTEN,
Executive Committee.

New York, June 23, 1904.

SULFURIC ACID (Continued)

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
25	1.2083	41.7	28.28	75.36	30.34	22.87
26	1.2185	43.7	29.53	76.00	31.69	24.08
27	1.2288	45.8	30.79	76.64	33.04	25.32
28	1.2393	47.9	32.05	77.30	34.39	26.58
29	1.2500	50.0	33.33	77.96	35.76	27.88
30	1.2609	52.2	34.63	78.64	37.16	29.22
31	1.2719	54.4	35.93	79.33	38.55	30.58
32	1.2832	56.6	37.26	80.03	39.98	32.00
33	1.2946	58.9	38.58	80.74	41.40	33.42
34	1.3063	61.3	39.92	81.47	42.83	34.90
35	1.3182	63.6	41.27	82.22	44.28	36.41
36	1.3303	66.1	42.63	82.97	45.74	37.95
37	1.3426	68.5	43.99	83.74	47.20	39.53
38	1.3551	71.0	45.35	84.52	48.66	41.13
39	1.3679	73.6	46.72	85.32	50.13	42.77
40	1.3810	76.2	48.10	86.13	51.61	44.45
41	1.3942	78.8	49.47	86.96	53.08	46.16
42	1.4078	81.6	50.87	87.80	54.58	47.92
43	1.4216	84.3	52.26	88.67	56.07	49.72
44	1.4356	87.1	53.66	89.54	57.58	51.56
45	1.4500	90.0	55.07	90.44	59.09	53.44
46	1.4646	92.9	56.48	91.35	60.60	55.36
47	1.4796	95.9	57.90	92.28	62.13	57.33
48	1.4948	99.0	59.32	93.23	63.65	59.34
49	1.5104	102.1	60.75	94.20	65.18	61.40
50	1.5263	105.3	62.18	95.20	66.72	63.52
51	1.5426	108.5	63.66	96.21	68.31	65.72
52	1.5591	111.8	65.13	97.24	69.89	67.96
53	1.5761	115.2	66.63	98.30	71.50	70.28
54	1.5934	118.7	68.13	99.38	73.11	72.66
55	1.6111	122.2	69.65	100.48	74.74	75.10
56	1.6292	125.8	71.17	101.61	76.37	77.60
57	1.6477	129.5	72.75	102.77	78.07	80.23
58	1.6667	133.3	74.36	103.95	79.79	82.95
59	1.6860	137.2	75.99	105.16	81.54	85.75

SULFURIC ACID (Continued)

Degrees Baumé.	* Freezing (Melting) Point. °F.	Per Cent 60° Baumé.	Pounds 60° Baumé in 1 Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in 1 Cubic Foot.
25	−23				
26	−30				
27	−39				
28	−49				
29	−61				
30	−74				
31	−82				
32	−96				
33	−97				
34	−91				
35	−81				
36	−70				
37	−60				
38	−53				
39	−47				
40	−41	61.93	53.34	77.36	66.63
41	−35	63.69	55.39	79.56	69.19
42	−31	65.50	57.50	81.81	71.83
43	−27	67.28	59.66	84.05	74.53
44	−23	69.09	61.86	86.30	77.27
45	−20	70.90	64.12	88.56	80.10
46	−14	72.72	66.43	90.83	82.98
47	−15	74.55	68.79	93.12	85.93
48	−18	76.37	71.20	95.40	88.94
49	−22	78.22	73.68	97.70	92.03
50	−27	80.06	76.21	100.00	95.20
51	−33	81.96	78.85	102.38	98.50
52	−39	83.86	81.54	104.74	101.85
53	−49	85.79	84.33	107.15	105.33
54	−59	87.72	87.17	109.57	108.89
55	..	89.67	90.10	112.01	112.55
56	..	91.63	93.11	114.46	116.30
57	..	93.67	96.26	117.00	120.24
58	..	95.74	99.52	119.59	124.31
59	− 7	97.84	102.89	122.21	128.52

Below 40

ALLOWANCE FOR TEMPERATURE

At 10°	Bé.	.029° Bé. or	.00023 Sp. Gr.	= 1° F.
" 20°	"	.036°	" .00034 "	= 1° "
" 30°	"	.035°	" .00039 "	= 1° "
" 40°	"	.031°	" .00041 "	= 1° "
" 50°	"	.028°	" .00045 "	= 1° "
" 60°	"	.026°	" .00053 "	= 1° "
" 63°	"	.026°	" .00057 "	= 1° "
" 66°	"	.0235°	" .00054 "	= 1° "

SULFURIC ACID (Continued)

Degrees Baumé.	Specific Gravity $\frac{60°\ F.}{60°}$	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
60	1.7059	141.2	77.67	106.40	83.35	88.68
61	1.7262	145.2	79.43	107.66	85.23	91.76
62	1.7470	149.4	81.30	108.96	87.24	95.06
63	1.7683	153.7	83.34	110.29	89.43	98.63
64	1.7901	158.0	85.66	111.65	91.92	102.63
64¼	1.7957	159.1	86.33	112.00	92.64	103.75
64½	1.8012	160.2	87.04	112.34	93.40	104.93
64¾	1.8068	161.4	87.81	112.69	94.23	106.19
65	1.8125	162.5	88.65	113.05	95.13	107.54
65¼	1.8182	163.6	89.55	113.40	96.10	108.97
65½	1.8239	164.8	90.60	113.76	97.22	110.60
65¾	1.8297	165.9	91.80	114.12	98.51	112.42
66	1.8354	167.1	93.19	114.47	100.00	114.47

Degrees Baumé.	Freezing (Melting) Point.	Per Cent 60° Baumé.	Pounds 60° Baumé in Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in Cubic Foot.	
60	+12.6	100.00	106.40	124.91	132.91	
61	27.3	102.27	110.10	127.74	137.52	
62	39.1	104.67	114.05	130.75	142.47	
63	46.1	107.30	118.34	134.03	147.82	
64	46.4	110.29	123.14	137.76	153.81	
64¼	43.6	111.15	124.49	138.84	155.50	
64½	41.1	112.06	125.89	139.98	157.25	
64¾	37.9	113.05	127.40	141.22	159.14	
65	33.1	114.14	129.03	142.57	161.17	
65¼	24.6	115.30	130.75	144.02	163.32	
65½	13.4	116.65	132.70	145.71	165.76	
65¾	− 1	118.19	134.88	147.63	168.48	
66	−29	119.98	137.34	149.87	171.56	

XI.—SULPHURIC ACID TABLE

94–100% H_2SO_4

By H. B. Bishop

Bé.	Sp. Gr. at 60° F.	Per Cent. H_2SO_4	Wt. 1 Cu. Ft.	Allowance for Temperature.
66	1.8354	93.19	114.47	At 94% .00054 sp.gr. = 1° F.
66.12	1.8381	94.00	114.64	" 96 .0053 " = 1° F.
66.23	1.8407	95.00	114.80	" 97.5 .00052 " = 1° F.
66.31	1.8427	96.00	114.93	" 100 .00052 " = 1° F.
66.36	1.8437	97.00	114.99	
66.36	1.8439	97.50	114.99	
66.36	1.8437	98.00	114.99	
66.30	1.8424	99.00	114.91	
66.16	1.8391	100.00	114.70	

FUMING SULFURIC ACID EQUIVALENTS

Total SO_3	Equivalent H_2SO_4	Per Cent H_2SO_4	Per Cent Free SO_3	Total SO_3	Equivalent H_2SO_4	Per Cent H_2SO_4	Per Cent Free SO_3
81.63	100.00	100	0	90.82	111.25	50	50
81.82	100.23	99	1	91.00	111.48	49	51
82.00	100.45	98	2	91.18	111.70	48	52
82.18	100.67	97	3	91.37	111.93	47	53
82.37	100.90	96	4	91.55	112.15	46	54
82.55	101.13	95	5	91.73	112.37	45	55
82.73	101.35	94	6	91.92	112.60	44	56
82.92	101.58	93	7	92.10	112.82	43	57
83.10	101.80	92	8	92.29	113.05	42	58
83.29	102.03	91	9	92.47	113.28	41	59
83.47	102.25	90	11	92.65	113.50	40	60
83.65	102.47	89	11	92.84	113.73	39	61
83.84	102.70	88	12	93.02	113.95	38	62
84.02	102.92	87	13	93.20	114.17	37	63
84.20	103.15	86	14	93.39	114.40	36	64
84.39	103.38	85	15	93.57	114.62	35	65
84.57	103.60	84	16	93.76	114.85	34	66
84.75	103.82	83	17	93.94	115.08	33	67
84.94	104.05	82	18	94.12	115.30	32	68
85.12	104.27	81	19	94.31	115.53	31	69
85 31	104.50	80	20	94.49	115.75	30	70
85.49	104.73	79	21	94.67	115.97	29	71
85.67	104.95	78	22	94.86	116.20	28	72
85.86	105.18	77	23	95.04	116.42	27	73
86.04	105.40	76	24	95.22	116.65	26	74
86.22	105.62	75	25	95.41	116.88	25	75
86.41	105.85	74	26	95.59	117.10	24	76
86.59	106.07	73	27	95.78	117.33	23	77
86.78	106.30	72	28	95.96	117.55	22	78
86.96	106.53	71	29	96.14	117.77	21	79
87.14	106.75	70	30	96.33	118.00	20	80
87.33	106.98	69	31	96.51	118.22	19	81
87.51	107.20	68	32	96.69	118.45	18	82
87.69	107.42	67	33	96.88	118.68	17	83
87.88	107.65	66	34	97.06	118.90	16	84
88.06	107.87	65	35	97.25	119.13	15	85
88.24	108.10	64	36	97.43	119.35	14	86
88.43	108.33	63	37	97.61	119.57	13	87
88.61	108.55	62	38	97.80	119.80	12	88
88.80	108.78	61	39	97.98	120.03	11	89
88.98	109.00	60	40	98.16	120.25	10	90
89.16	109.22	59	41	98.35	120.48	9	91
89.35	109.45	58	42	98.53	120.70	8	92
89.53	109.67	57	43	98.71	120.92	7	93
89.71	109.90	56	44	98.90	121.15	6	94
89.90	110.13	55	45	99.08	121.37	5	95
90.08	110.35	54	46	99.27	121.60	4	96
90.27	110.58	53	47	99.45	121.83	3	97
90.45	110.80	52	48	99.63	122.05	2	98
90.63	111.02	51	49	99.82	122.28	1	99
				100.00	122.50	0	100

Compiled from the table by H. B. Bishop, Van Nostrand's Chemical Annual, 1913.

METHOD OF ANALYSIS OF CHLOROSULFONIC ACID

Chlorosulfonic acid, $SO_3 \cdot HCl$, decomposes to H_2SO_4 and HCl on addition of water, the reaction being violent. Considerable care must be exercised to prevent loss of acid during dilution with water for examination of the product. The following method of analysis has been found satisfactory:

Total Acidity.—Three to four grams of the chlorosulfonic acid are weighed in a Déli tube or small glass bulb. About 25 ml. of distilled (neutral) water and about 10 ml. less NaOH (normal strength) than is necessary to neutralize the sample (i.e., $\frac{\text{weight sample} - 10}{0.04001} = \text{ml. NaOH to be taken}$) are placed in a heavy wall glass bottle (250–300 ml. capacity). If the sample is weighed in a Déli tube it is run into the NaOH solution according to the procedure described on page 506. If the bulb is used, the bottle, with the sample inserted, is stoppered, wrapped in a towel and shaken vigorously until the bulb breaks and the acid mixes with the water and NaOH. The excess of acid is now titrated with N NaOH, using phenolphthalein or methyl red indicator. The total acidity is calculated to SO_3 and recorded as % SO_3.

Titration of Chloride.—The NaCl formed is titrated with N/3 $AgNO_3$ solution, using K_2CrO_4 indicator. The ml. of the reagent are calculated to the equivalent HCl. Since NaOH is apt to contain NaCl, the blank is subtracted to obtain the true HCl equivalent in the sample. The % HCl is calculated.

The Composition of the Acid is now determined as follows:

(*a*) Total acid as % $SO_3 = a$.

(*b*) HCl obtained by titration of the neutralized solution (made faintly acid) with N/3 $AgNO_3$ (the HCl blank for the NaOH used in (*a*) having been subtracted) $= b$. The HCl is converted to its equivalent SO_3 by multiplying by $1.0978 = b'$.

(*c*) SO_3 (combined and free). The SO_3 equivalent of HCl obtained in *b* is subtracted from the total acidity as SO_3 of (*a*) is $a - b' = SO_3$ total.

(*d*) $100 - (\%\ SO_3 + \%\ HCl) = \%\ H_2O$ in sample. This is combined with a protion of the SO_3 as H_2SO_4. Calculate to % H_2SO_4 by multiplying by 5.4444. Allowance must be made for impurities if present.[17]

(*e*) The SO_3 combined with H_2O is subtracted from the total SO_3 of (*c*). The result is the SO_3 of the chlorosulfonic acid and free SO_3 (if any).

By inspection it is possible to ascertain whether the product contains free SO_3 or free HCl since $SO_3 \cdot HCl$ are in the proportion 31.29% HCl and 68.71% SO_3, i.e., HCl : SO_3:: 1 : 2.2.

If SO_3 is in excess. The HCl is calculated to $SO_3 \cdot HCl$ by multiplying by 3.1956, the result is the *per cent chlorosulfonic acid* in the sample.

Free SO_3 is obtained by subtracting % $SO_3 \cdot HCl + \%\ H_2SO_4$ from 100.

If HCl is in excess. The % SO_3 obtained in (*e*) is multiplied by 1.4555; the result is the *per cent chlorosulfonic acid.*

Free HCl is obtained by subtracting % $SO_3 \cdot HCl + \%\ H_2SO_4$ from 100.

Results are reported as % $SO_3 \cdot HCl$, H_2SO_4, free SO_3 or free HCl.

[17] (100—impurities non-titratable)—(%SO_3+%HCl) = %H_2O.

Factors:

$HCl \times 1.0978 = SO_3$, $HCl \times 3.1956 = SO_3 \cdot HCl$ and $HCl \times 2.1959 = SO_3$ in SO_3HCl.
$SO_3 \times 0.8998 = HCl$, $SO_3 \times 1.4555 = SO_3 \cdot HCl$ and $SO_3 \times 0.4554 = HCl$ in SO_3HCl.
$H_2O \times 5.4444 = H_2SO_4$, $H_3SO_4 \times 0.1837 = H_2O$, $H_2SO_4 \times 0.7436 = HCl$.
$NaCl \times 0.6238 = HCl$, $SO_3 \cdot HCl = 31.29\%$ HCl and 68.71% SO_3.

VOLUMETRIC ESTIMATION OF FREE ACID IN PRESENCE OF IRON SALTS

The red precipitate formed when solutions containing iron are titrated with caustic makes it difficult to detect the end-point of neutralization; the method suggested by C. A. Ahlum [18] takes advantage of the white compound formed by precipitating the iron as a phosphate and the fact that monosodium phosphate is neutral to methyl-orange indicator.

Reactions

$Fe_2(SO_4)_3 + 2NaH_2PO_4 + x$ free acid $= 2FePO_4 + Na_2SO_4 + x$ free acid $+ 2H_2SO_4$,
or $2FeCl_3 + 2NaH_2PO_4 + x$ free acid $= 2FePO_4 + 2NaCl + x$ free acid $+ 4HCl$.

The acid equivalent to ferric iron is deducted from the total acid found, the excess acid being due to the free acid in the solution.

Procedure.—To the solution containing the iron and free acid is added an excess of c.p. solution of monosodium phosphate (neutral to methyl-orange), and then a few drops of the indicator. The acidity of the solution is now determined by titration with standard caustic in the usual way, the solution being cold. From this titration the total free and combined acid are calculated.

Iron is now determined in a separate portion by titration with stannous chloride or dichromate.

Calculation.

(A) $Fe_2O_3 \times 1.2285 =$ g. H_2SO_4 (combined).
$Fe_2O_3 \times 0.9135 =$ g. HCl (combined).

(B) One ml. N/5 NaOH = .00981 gram H_2SO_4 or .00729 gram HCl.
Total acid (B) minus combined acid (A) = *free acid.*

Determination of Boric Acid in Borates

The details of procedure for the determination of boric acid are given in the chapter on Boron in Volume I. The method takes advantage of the fact that boric acid is a weak acid having an end-point in an alkalimetric titration of pH 10–11 hence cannot be titrated in presence of indicators having a lower pH range, such as methyl red or methyl orange, pH 3.1–6.3. It is possible, therefore, to liberate boric acid from its combination by means of a mineral acid, titrate or neutralize the mineral acid with NaOH in presence of methyl red or

[18] C. A. Ahlum, The Analyst, **31**, 168 (1906).

methyl orange and then titrate boric acid in presence of phenolphthalein indicator after the addition of a polyhydric alcohol, such as glycerol or mannitol.

The borate is first converted to a soluble sodium salt by transposition by means of sodium carbonate and extraction with water or the boric acid is set free by boiling with a mineral acid, using a reflux condenser to prevent loss of boric acid, which is volatile with steam. If sodium carbonate treatment is used the CO_2 must be expelled by acidifying and heating for a few minutes in a covered beaker avoiding vigorous boiling. The free mineral acid is now neutralized with NaOH in presence of methyl orange or methyl red indicator. Neutral glycerol is added in sufficient quantity (25 ml. is sufficient for 0.5 g. B_2O_3) and again the solution is neutralized if an acidity is evident from the glycerol addition (commercial glycerol is apt to contain free acid). Phenolphthalein indicator is added and the boric acid titrated with standard NaOH until a reddish pink color of the combined indicators is obtained.

The solution titrated and the reagents used must be free from CO_2, iron, aluminum and products other than boric acid, that would react with the alkali in the titration.

1 ml. of 1 N NaOH is equivalent to 0.03482 g. B_2O_3.

ORGANIC ACIDS

Titrations of organic acids are made preferably with phenolphthalein. Methyl orange cannot be used. The water used for diluting the organic acid must be free of carbon dioxide.

ANALYSIS OF FORMIC ACID

Formic acid occurs in solutions of varying strength, i.e., 30, 50, 75, 90%, etc. The impurities that are frequently present are sulfuric and hydrochloric acid. If formic acid alone is present it may be determined by direct titration. 1 ml. N/10 NaOH = 0.004602 gram formic acid In presence of other acids the following method is recommended.

Procedure.—About 10 grams of the sample weighed in a tared bottle (Blay-Burkhard form is convenient) is run into about 200 ml. of distilled water in a graduated flask of 500 ml. capacity and made to volume. 50 ml. of this diluted sample pipetted into an Erlenmeyer flask is made alkaline with Na_2CO_3 solution. After warming a measured excess of N/10 $KMnO_4$ is added. Formic acid is oxidized to $H_2O + CO_2$ and a precipitate of MnO_2 is thrown down. 10 ml. of dilute H_2SO_4 are added and a measured volume of N/10 oxalic acid is added until all of the precipitate has dissolved and the permanganate color has disappeared. The excess of oxalic acid is now titrated with N/10 permanganate reagent. From this the ml. $KMnO_4$ required by the formic acid is obtained.

1 ml. N/10 $KMnO_4$ = 0.002301 gram formic acid.

The equivalent ml. values of the $KMnO_4$ and $H_2C_2O_4$ should be obtained by titration.

Sulfuric Acid.—This is conveniently determined on about a 20 gram sample diluted to 200 ml. by precipitation with $BaCl_2$ according to the standard procedure.

$$BaSO_4 \times 0.4202 = H_2SO_4.$$

Hydrochloric Acid.—This may be determined on a 20 gram sample by precipitation with $AgNO_3$ in presence of 5 ml. conc. HNO_3, the sample having been diluted to about 200 ml.

$$AgCl \times 0.2545 = HCl.$$

ANALYSIS OF ACETIC ANHYDRIDE—ACIDITY METHOD

Acetic anhydride $\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O$ is a volatile, colorless liquid, possessing a characteristic sharp penetrating odor. The vapor is very irritating to the nose and eyes. The pure anhydride boils at 137° C. Mixed with water strong acetic anhydride settles out into a distinct layer very similar to carbon disulfide. It hydrolyzes slowly forming a solution of acetic acid. When below 50% in strength (the diluting liquid being acetic acid) the product mixes readily with water at ordinary temperatures (20° C.). Distinct separation from water takes place when the strength of the anhydride is over 55%, the product being added to the water dropwise. The separation becomes more decided with increase of the percentage of anhydride.

The analysis consists in titrating the acetic acid formed by the hydrolysis of the anhydride. Since the product is volatile it is weighed in stoppered bottles. Low results are obtained if sufficient time is not allowed for complete hydrolysis.

Procedure.—A sample of approximately 5 to 5.5 grams is weighed in a bottle 6 to 8 ml. in capacity. A small 2-dram apothecaries' bottle with No. 00 rubber stopper is satisfactory. The stopper is fitted loosely and the bottle containing the sample is immersed in 100 ml. of normal NaOH and 300 ml. of distilled water in a 500-ml. "salt mouth" bottle with rubber stopper. The bottle is closed tightly and shaken to free the small rubber stopper from the weighing bottle, and permit the sample to mix with the reagent. After hydrolyzing for at least one hour the sample is titrated with N/5 H_2SO_4 to determine the excess of N/1 NaOH, using phenolphthalein indicator.

Calculation.

$$\frac{\text{ml. NaOH} \times 0.06003}{\text{wt. sample}} \times 100 = \%\ CH_3COOH$$

$$(\%\ CH_3COOH - 100) \times 5.665 = \%\ (CH_3CO)_2O.$$

Example.—If the sample titrated 101% CH_3COOH then

$$(101 - 100) \times 5.665 = 5.665\%\ (CH_3CO)_2O.$$

NOTES.—100 per cent $(CH_3CO)_2O = 117.65\%\ CH_3COOH$.

$$\text{Per cent Anhydride} = \frac{A - 100}{117.65 - 100} \times 100$$

$$= (A - 100)5.665.$$

$A = \%CH_3COOH$ by titration.

$$H_2SO_4 \times 1.2241 = CH_3COOH.$$

DETERMINATION OF ACETIC ANHYDRIDE—ANILINE METHOD

Procedure.—The analysis should be carried out in duplicate runs, each portion being determined as follows: Two ml. of anhydride are run from a burette into a tared 5 ml. weighing bottle and carefully weighed, the bottle being stoppered. The sample is now placed in an Erlenmeyer flask containing 50 ml. N NaOH and 50 ml. distilled water, the stopper of the bottle being loosened so that the anhydride mixes with the alkali. After forty minutes with occasional shaking of the flask to assist the mixing, the residual NaOH is titrated with N H_2SO_4, in presence of phenolphthalein indicator, 2 or 3 ml. of acid added in excess. After standing fifteen minutes longer the excess acid is titrated back with N/10 NaOH. From the amount of N NaOH required by the anhydride calculate the amount of N NaOH required by 100 grams of the sample. Record this as " A."

Twenty ml. of recently redistilled, perfectly dry aniline are run into a 50 ml. tared weighing bottle and 2 ml. of the anhydride added from a burette. The sample is added slowly, swirling the aniline to get an equal distribution. When the mixture has cooled to room temperature the weight of the anhydride is determined (the aniline and bottle having previously been weighed). After an hour the mixture is transferred to a 500 ml. volumetric flask and the solution diluted to mark with neutral alcohol and distilled water (1 : 1). Fifty ml. of this solution are titrated with N/10 NaOH. From the number of ml. required calculate the ml. N NaOH corresponding to the residual acetic acid from 100 grams of the sample. Record this as " B."

Then A–B corresponds to one half the anhydride in 100 grams of the sample This value multiplied by 0.10207 = per cent acetic anhydride.

0.10207 = molecular weight of acetic anhydride divided by 1000.

Correction for Mineral Acids if Present.—In weighed portions (10 grams) determine hydrochloric acid by precipitation with $AgNO_3$ and sulfuric acid by precipitation with $BaCl_2$ in the usual way, the samples having hydrolyzed in 100 ml. portions of water. From the percentages of mineral acids present calculate to ml. normal equivalents and deduct from the titrations above, or calculate the anhydride equivalent and make deduction.

1 ml. N H_2SO_4 = .04904 g. 1 ml. N HCl = .03647 g. 1 ml. N CH_3COOH = .06003 g. $CH_3COOH \times 0.85 = (CH_3CO)_2O$,

$H_2SO_4 \times 1.0404 = (CH_3CO)_2O$, $HCl \times 1.3889 = (CH_3CO)_2O$.

ANALYSIS OF ACETIC ACID

The acidity of acetic acid may be determined by titration with standard caustic, using phenolphthalein as indicator.

About 4 to 5 grams of glacial acetic acid or a corresponding amount of dilute acid are taken for analysis, being weighed out in a weighing bottle or other suitable container used for strong and weak acids. The acid is mixed with about 250 ml. of water and titrated in the presence of phenolphthalein indicator with normal caustic.

One ml. N/1 NaOH = 0.06005 gram CH_3COOH.

Impurities in Acetic Acid

The more important impurities that are looked for in commercial acetic acid are formic acid, furfurol, acetone, sulfuric acid, sulfurous acid, hydrochloric acid, metals.

In the examination of the acid the physical appearance—turbidity and color are noted.

Formic Acid in Acetic

Qualitative.—Ten ml. of the acid (glacial diluted 1 : 10) are heated with 1 gram of sodium acetate and 5 ml. of 5% mercuric chloride solution. A turbidity indicates formic acid.

Quantitative.—Five grams of glacial acetic acid or corresponding quantity of dilute acid are treated with 5 grams of sodium acetate and 40 ml. of mercuric chloride solution (5%) and 30 ml. of water added. The mixture is heated for two hours in a flask with a return condenser, the flask being surrounded by steam. The precipitated mercurous chloride, HgCl, is filtered off, dried and weighed.

Weight of HgCl $\times$ 0.0977 = formic acid equivalent.

Furfurol in Acetic Acid

Qualitative.—Aniline dissolved in pure glacial acetic acid (5 ml. aniline in 2 ml. glacial acetic acid) and added to 100 ml. of the sample will produce a red color in presence of furfurol.

Quantitative.—The test may be made quantitative by comparing the color produced with standard solutions containing known amounts of furfurol. One gram of redistilled furfurol is dissolved in 100 ml. of 95% alcohol. 1 ml. of this solution is diluted to 100 ml. with 95% alcohol. 1 ml. = 0.0001 gram of the reagent.

Test for furfurol in vinegar. Fifty ml. of the vinegar is neutralized with sodium hydroxide, and 15 to 20 ml. are distilled. Two ml. of colorless aniline and 15 ml. of hydrochloric acid (1 : 12) added. The mixture is warmed to about 15° C. for a few minutes and the color compared with standards prepared in the same way.

Gravimetric Method with Phloroglucid

Place a quantity of the material, chosen so that the weight of phloroglucid obtained shall not exceed 0.300 gram, in a flask, together with 100 ml. of 12% hydrochloric acid (specific gravity, 1.06), and several pieces of recently heated pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat, rather gently at first, and so regulate as to distill over 30 ml. in about ten minutes, the distillate passing through a small filter paper. Replace the 30 ml. driven over by a like quantity of the dilute acid added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 ml. To the completed distillate gradually add a quantity of phloroglucol (purified if necessary) dissolved in 12% hydrochloric acid and thoroughly stir

the resulting mixture. The amount of phloroglucol used should be about double that of the furfural expected. The solution first turns yellow, then green, and very soon an amorphous greenish precipitate appears, which grows rapidly darker, till it finally becomes almost black. Make the solution up to 400 ml. with 12% hydrochloric acid, and allow to stand overnight.

Filter the amorphous black precipitate into a tared Gooch crucible through an asbestos felt, wash carefully with 150 ml. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for four hours at the temperature of boiling water, cool and weigh, in a weighing bottle, the increase in weight being reckoned as phloroglucid. To calculate the furfural, pentose, or pentosan from the phloroglucid, use the following formulas given by Kröber:

(*a*) For weight of phloroglucid " a " under 0.03 gram.

Furfural $=(a+0.0052)\times 0.5170$.
Pentoses $=(a+0.0052)\times 1.0170$.
Pentosans $=(a+0.0052)\times 0.8949$.

(*b*) For weight of phloroglucid " a " over 0.300 gram.

Furfural $=(a\%0.0052)\times 0.5180$.
Pentoses $=(a+0.0052)\times 1.0026$.
Pentosans $=(a+0.0052)\times 0.8824$.

For weight of phloroglucid " a " from 0.03 to 0.300 gram use Kröber's table of the following formulas:

Furfural $=(a+0.0052)\times 0.5185$.
Pentoses $=(a+0.0052)\times 1.0075$.
Pentosans $=(a+0.0052)\times 0.8866$.

The phloroglucol is purified by recrystallization from hydrochloric acid. For details of the procedure see Bulletin 107, U. S. Dept. of Agriculture, Bureau of Chemistry. (1912, page 54.)

Acetone in Acetic Acid

Fifteen grams of glacial acetic acid, or a corresponding amount of weak acid, is treated with 70 ml. potassium hydroxide (10% solution), or sufficient caustic to make the solution slightly alkaline. The solution is cooled and 25 ml. N/5 iodine solution added and sufficient hydrochloric acid to make the mixture faintly acid. The excess of iodine is titrated with N/5 sodium thiosulfate, using starch indicator. The total iodine solution taken minus the equivalent ml. of thiosulfate = the iodine combined with the acetone, then the weight of iodine in grams multiplied by 0.07612 = grams acetone in the sample.

Sulfuric Acid in Acetic Acid

This is best determined by the turbidity test. About 5 ml. of the sample are taken and 1 drop of hydrochloric acid and half a ml. of 10% barium chloride. The turbidity is now compared with a standard pure acetic acid solution containing a known quantity of $BaSO_4$, the standard being added to a comparison

cylinder until the turbidity is the same as that of the sample, which has been diluted to a convenient volume in a Nessler tube or similar comparison cylinder. The apparatus used in determining small amounts of titanium, lead, etc., is suitable for this test. In this case the glowing wire or filament of an incandescent light is viewed through the solutions, the brightness of the wire acting as a guide in matching the solutions.

Sulfurous Acid in Acetic Acid

This is best detected by placing in a small flask about 20 ml. of the sample, adding 5 ml. of strong hydrochloric acid and about 3 grams of zinc and covering with a filter paper saturated with lead acetate. The blackening of the paper indicates SO_2 in the sample (e.g., reduced to H_2S by the hydrogen generated by the zinc).

The sulfurous acid is best titrated with N/10 iodine solution, using starch indicator. 1 ml. N/10 I_2 = .0032 gr. SO_2.

Hydrochloric Acid in Acetic Acid

Determined by the turbidity test as in case of sulfuric acid, silver nitrate solution being used to precipitate AgCl, and nitric acid substituted for hydrochloric acid.

Metals in Acetic Acid

Total Solids.—Ten to 100 grams of the acid is evaporated to dryness in a platinum dish. The residue contains the non-volatile solids.

ACETATES

Two to 5 grams of the material is placed in a Kjeldahl flask connected by means of a condenser to a receiving flask containing half normal caustic. About 20 ml. of 85% phosphoric acid are added and about 150 ml. of water. Gentle heat is applied and gradually increased. About 100 ml. of the solution is distilled into the caustic. Additional hot water is added to the residue in the Kjeldahl flask and the distillation continued. This is repeated until about 800 ml. of solution has been distilled over. The CO_2 is boiled out of the distillate, a reflux condenser being used to prevent loss of the acetic acid. If the solution is alkaline, a known amount of acid is added and the CO_2 boiled out. The excess acid is now titrated and the amount of acetic acid in the distillate calculated.

One ml. N/2 NaOH = 0.030015 gram CH_3COOH

$CH_3COOH \times 1.3169 = Ca(CH_3CO_2)_2$, or $\times 1.3663 = CH_2COONa$.

Acetates of the Alkalies and Alkaline Earths.—In absence of other organic acids, nitrates, etc., a quick method is suggested by Sutton (Vol. Analy., X. Ed., p. 91). The salts are converted into carbonates by ignition and the residue titrated with normal acid.

One ml. N/1 acid = 0.06003 gram CH_3COOH.

ACETIC ACID AT 15°

OUDEMANS

Specific Gravity.	Per Cent $HC_2H_3O_2$.	Specific Gravity.	Per Cent $HC_2H_3O_2$.	Specific Gravity.	Per Cent $HC_2H_3O_2$.	Specific Gravity.	Per Cent $HC_2H_3O_2$.
0 9992	0	1.0363	26	1.0623	51	1 0747	76
1 0007	1	1.0375	27	1 0631	52	1.0748	77
1.0022	2	1.0388	28	1 0638	53	1.0748	78
1.0037	3	1 0400	29	1 0646	54	1.0748	79
1 0052	4	1.0412	30	1.0653	55	1 0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1 0746	82
1.0098	7	1 0447	33	1.0673	58	1 0744	83
1.0113	8	1.0459	34	1.0679	59	1 0742	84
1.0127	9	1 0470	35	1 0685	60	1.0739	85
1.0142	10	1 0481	36	1.0691	61	1.0736	86
1.0157	11	1 0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1 0702	63	1 0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1 0523	40	1.0712	65	1 0713	90
1.0214	15	1.0533	41	1.0717	66	1 0705	91
1.0228	16	1.0543	42	1.0721	67	1 0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1 0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1 0553	100
1.0350	25						

CARBONIC ACID

FREE CARBONIC ACID IN AQUEOUS SOLUTION

The method is based on the reaction

$$H_2CO_3 + Ba(OH)_2 = BaCO_3 + 2H_2O.$$

Procedure.—An excess of standard barium hydroxide solution is added to the water containing the carbonic acid. Barium carbonate is precipitated as shown in the reaction above. The excess of $Ba(OH)_2$ is now titrated with standard hydrochloric acid, using phenolphthalein indicator.

1 ml. N/10 $Ba(OH)_2$ or 1 ml. N/10 HCl is equivalent to 0.0022 g. CO_2.

CARBONIC ACID PRESENT AS BICARBONATE

Reaction.—$NaHCO_3 + HCl = NaCl + H_2O + CO_2$.

Procedure.—The solution is titrated with standard HCl, using methyl orange indicator.

1 ml. N/10 HCl = 0.0044 g. CO_2.

Carbonic Acid Present as Carbonate

Reaction.—$Na_2CO_3+2HCl=2NaCl+H_2O+CO_2$.

Procedure.—The solution is titrated with standard HCl, using methyl orange indicator. Carbonates of barium, strontium, calcium and magnesium are titrated with an excess of hydrochloric acid and this excess determined with standard alkali.

1 ml. N/10 HCl = 0.0022 g. CO_2.

CITRIC ACID

The free acid may be titrated with sodium hydroxide, using phenolphthalein indicator. One ml. N/1 alkali = 0.07 gram crystallized citric acid.

VOLUMETRIC DETERMINATION OF OXALIC ACID

Permanganate Method

About 3 grams of the oxalic acid or its salt are dissolved in 200 ml. of CO_2 free water and 50 ml. 2N sulfuric acid added. The solution is heated to about 70° C. and titrated with standard, normal solution of potassium permanganate, to a faint pink, persisting for three minutes.

1 ml. N/$KMnO_4$ = 0.04501 g. $H_2C_2O_4$ or 0.06302 g. $H_2C_2O_4 \cdot 2H_2O$.

The acid may also be titrated with standard caustic solution. Titration is made in a hot solution, using phenolphthalein indicator.

DETERMINATION OF PHENOL (CARBOLIC ACID)

Bromine reacts with an aqueous solution of phenol decomposing it to the water insoluble tribromophenol and forming hydrobromic acid as shown in the reaction

$$C_6H_5OH+3Br_2=C_6H_2Br_3(OH)+3HBr.$$

The excess of bromine is determined by adding potassium iodide solution and determining the liberated iodine by titration with standard thiosulfate. The method is applicable only to pure preparations of carbolic acid.

Reagent: ***Standard Bromine.***—A solution of free bromine in water cannot be kept. The reagent may be prepared, however, by adding a definite amount of bromate to a bromide solution, which on acidification, will liberate a definite amount of bromine according to the reaction $KBrO_3+5KBr+6HCl=3Br_2+6KCl+3H_2O$. The acid is added only to the portions of the reagent used for the tests. In preparing a N/10 solution 2.784 grams of pure dry potassium bromate and 10 grams of potassium bromide are dissolved in a little water and diluted to 1000 ml.

Procedure.—0.5 gram of phenol is dissolved in a little water and diluted to 1000 ml. To 100 ml. of this, equivalent to 0.05 g. of sample, are added (in a stoppered bottle) 50 ml. of the bromate solution and the mixture shaken. 5 ml. of concentrated HCl are now added, the solution again shaken and after 15 minutes 2 grams of potassium iodide are added. The liberated iodine is titrated in presence of starch solution with N/10 thiosulfate.

1 ml. N/10 $KBrO_3$ = 0.001567 g. C_6H_5OH.

TARTARIC ACID

Tartaric acid, cream of tartar, Rochelle salt, tartar emetic, normal potassium tartrate, iron tartrate and other salts of tartaric acid are obtained from the residues of wine manufacture. The raw materials consist of lees, tartars, calcium tartrate. Tartaric acid is present in these residues in the form of potassium hydrogen tartrate (vitartrate of potassium) or as normal calcium tartrate. In the examination of the raw material for its evaluation total tartaric acid and that present as bitartrate are determined.

Estimation of Acid Potassium Tartrate—Oulman's Method

Procedure.—3.76 grams of the powdered tartar is placed in a liter flask, 750 ml. of water added, the solution heated to boiling and boiled for 4 to 5 minutes. Prolonged boiling is avoided, as changes may occur which would cause error in results. The flask is filled to the mark and allowed to cool. After readjusting to exactly one liter the solution is filtered through a dry filter and 500 ml. of this evaporated to dryness on the water-bath in a porcelain casserole. 5 ml. of water is added to moisten this residue and 100 ml. of 95% alcohol added on cooling. After standing half an hour the alcohol is decanted through a dry filter, allowed to drain and any potassium bitartrate on the filter is washed back into the dish with hot water. The solution is made up to about 100 ml. and titrated hot with N/5 KOH. A correction of 0.2 ml. is added for the loss of bitartrate in the alcohol.

Estimation of Total Tartaric Acid. Goldenberg Method

Procedure.—Six grams of the sample containing more than 45% of tartaric acid or 12 grams if it contains less than 45% are added to 18 ml. of hydrochloric acid (sp.gr. 1.1) and the mixture stirred 10 minutes. This is now transferred to a 200-ml. measuring flask and distilled water added to the mark. The well mixed solution is now filtered through a dry filter into a beaker. 100 ml. is pipetted out and added to 10 ml. of a solution of potassium carbonate containing 66 grams of the anhydrous salt per 100 ml. in a 300 ml. beaker. The beaker is covered by a clock glass and the solution boiled gently for twenty minutes; the calcium carbonate precipitates in a crystalline form during this heating. The solution is transferred to a 200 ml. measuring flask, made up to mark after cooling, and filtered through a dry filter.

100 ml. of the filtrate is evaporated in a porcelain casserole (or pyrex beaker) on the water bath until the volume is about 15 ml. To the hot solution 3.5 ml. of glacial aetic acid are added gradually with constant stirring and the mixture stirred for 5 minutes more after the addition. After standing 10 minutes 100 ml. of 95% alcohol are added and the mixture again stirred 5 minutes. Upon settling 10 minutes the precipitated bitartrate is filtered off, suction being applied. The precipitate is washed with alcohol until free of acid. (Test 30 ml. This should require the same titration with N/5 alkali with phenolphthalein indicator as 30 ml. of the alcohol used in the washing.) The precipitate on the filter is washed into a porcelain dish with 200 ml. of hot water and titrated hot with N/5 potassium or sodium hydroxide, using litmus paper as indicator.

The alkali is standardized against pure potassium hydrogen tartrate.

Corrections.—Deduct 0.3% for material containing less than 45% tartaric acid, 0.3% for raw material containing 45–60% and 0.2% for material containing 60–70%. No correction is made for better grades of material.

Impurities in Tartaric Acid

Iron and Alumina (alum).—These are determined in the ash of the ignited product, the ash being dissolved in hydrochloric acid. P_2O_5 may also be determined in this ash.

Arsenic.—This may be determined by the Gutzeit Method. (See chapter on Arsenic in Volume I.)

Lead.—This is determined by the colorimetric procedure given on page 517, Vol. I.

Free Sulfuric Acid in Tartaric Acid Liquors.—The solution 10 ml. or more is treated with ten times its volume of alcohol, and after settling overnight the mixture is filtered. Sulfuric acid is determined in the alcohol filtrate in the usual way.

ALKALIES

ANALYSIS OF SODIUM HYDROXIDE

Commercial caustic soda, purchased in blocks packed in iron drums, should be sampled with care. The hydroxide sets first on the outside, so that the impurities segregate towards the core of the block. In order to get a representative sample different sections of the block should be tapped. The material takes up moisture and carbon dioxide from the air, so that the surface of the sample should be removed before weighing. The weighing and dissolving of the sample should be done as rapidly as possible.

Procedure

Ten grams of the hydroxide are dissolved in water and the solution made up to exactly 500 ml. Aliquots of this solution are taken for the following determinations.

Total Alkali.—Fifty ml. of the caustic solution, equivalent to 1 gram of the solid, are titrated with N/H_2SO_4 in presence of methyl orange indicator, until the faint pink end-point is obtained.

1 ml. $N/H_2SO_4 = .031$ grams of Na_2O (total alkali actual).

Note.—In the New York and Liverpool test N/H_2SO_4 value is .032 g. NaOH per ml.

Sodium Hydroxide.—Fifty ml. of the sample is treated with 100 ml. of 10% $BaCl_2$ solution and the NaOH then titrated with N/H_2SO_4 in presence of phenolphthalein indicator.

$$1 \text{ ml. } N/H_2SO_4 = .04 \text{ gram NaOH.}$$

Sodium Carbonate.—Multiply the difference between the total alkali titration and the titration for NaOH by .053 the result is grams Na_2CO_3.

Alternative Methods. Sodium Hydroxide and Sodium Carbonate.—Carbon dioxide is readily picked up by NaOH so that it is invariably present in caustic soda forming sodium carbonate. The carbonate and hydrate may be determined in the same solution as follows.

Fifty ml. of the sample equivalent to one gram of the solid, are titrated with normal H_2SO_4, in presence of phenolphthalein, until the pink color just disappears. This occurs when all of the sodium hydroxide is neutralized and the carbonate has been converted to bicarbonate. This titration may be recorded as ml. *A*.

Methyl orange is now added and the titration continued until the yellow color changes to pink. This titration is recorded as ml. *B*.

Then $NaOH = (A - B) \times 0.04$ and $Na_2CO_3 = 2B \times 0.053$.

Determination of Impurities

Sodium Chloride.—This may be determined on 25 to 50 ml. (0.5–1 gram) of the above solution by Volhard's method described in Vol. I, page 271, or the method for NaCl in soda ash, page 2261, this volume.

$$1 \text{ ml. } N/20\ AgNO_3 = 0.002923 \text{ gram NaCl.}$$

Sodium Sulfate.—Fifty ml. of the solution equivalent to 1 gram of the solid are acidified with hydrochloric acid (H_2SO_4 free) and the sulfate precipitated from a boiling solution by addition of 10% $BaCl_2$ solution according to the standard procedure.

$$BaSO_4 \times 0.6086 = Na_2SO_4.$$

The following determinations are seldom required.

Sodium Silicate.—10 grams of the sample are dissolved in about 100 ml. of water and the solution acidified with hydrochloric acid. After evaporation to dryness the residue is taken up with water. Silica remains insoluble and is filtered off, washed, ignited and weighed. $SiO_2 \times 2.0282 = Na_2SiO_3$.

Sodium Aluminate.—The water extract from silica contains the alumina as soluble chloride. $Al(OH)_3$ may be precipitated with ammonia according to the standard procedure, then filtered off, washed, ignited and weighed as Al_2O_3. $Al_2O_3 \times 1.6067 = Na_2Al_2O_4$.

Insoluble Matter.—100 grams of the material is dissolved in a liter of water, phenolphthalein indicator is added and the solution almost neutralized with hydrochloric acid, the solution should be slightly alkaline. The sample is filtered and the residue of sand, Fe_2O_3, etc., weighed as insoluble matter. Caustic solutions attack filter paper so that it is advisable to partly neutralize the free alkali before filtration.

Water.—5 to 10 grams of the hydroxide are placed in a small Erlenmeyer flask, whose weight is known, a funnel is placed in the neck of the flask to prevent loss of the material and to prevent its absorbing carbon dioxide from the air. After placing in a sand bath the material is kept at about 150° C. for about four hours. It is now allowed to cool, the funnel remaining in the flask, and the loss of weight determined.

Determination of Strength of Caustic Liquors by the Hydrometer

The specific gravity of the liquor is taken by the hydrometer exactly as in case of acids. The strength of the liquor is ascertained by reference to the table on Sodium Hydroxide, page 2268.

Potassium Hydroxide

Analysis of potassium hydroxide is similar to that of sodium hydroxide. The following molecular weights will be of use in the calculations:

$KOH = 56.11$; $K_2CO_3 = 138.21$; $KCl = 74.56$; $K_2Al_2O_4 = 196.4$; $K_2SiO_3 = 154.5$.

Volumetric Determination of Carbonate in Sodium Bicarbonate [19]

$NaHCO_3$ in presence of $BaCl_2$ gives insoluble $BaCO_3$ and NaCl, neither subject to hydrolysis nor acting of phenolphthalein.

The $NaHCO_3$ to be analyzed is added to a solution of NaOH of known strength and $BaCl_2$ is added to the Na_2CO_3 formed. By determining the free NaOH, that which is combined with $NaHCO_3$ can be calculated and the equivalent $NaHCO_3$ thus determined.

Analysis and Testing of Impurities in Caustic Soda [20]

Reagents and Indicators: ***Water.***—The water used in the following methods should be distilled water, neutral to phenolphthalein and methyl orange indicators.

Hydrochloric Acid (1-1).—Dilute 500 ml. of colorless hydrochloric acid (HCl) of 1.19 specific gravity with an equal volume of distilled water.

Sulfuric Acid (1-3).—Into 3 liters of distilled water cautiously add with stirring 1 liter of colorless sulfuric acid (H_2SO_4) of 1.84 specific gravity.

Nitric Acid (1-4).—Into 4 liters of distilled water add with stirring 1 liter of colorless concentrated nitric acid (HNO_3).

Ammonium Hydroxide.—The ammonium hydroxide (NH_4OH) used should be a pure, clear, colorless solution of 0.90 specific gravity.

Ammonium Hydroxide (Dilute).—Dilute 100 ml. of ammonium hydroxide (NH_4OH) specific gravity 0.90 with 900 ml. of distilled water.

Ammonium Sulphide Solution.—This solution is prepared by passing hydrogen sulfide gas (H_2S) through a dilute ammonium hydroxide solution (NH_4OH) until the solution smells strongly of hydrogen sulfide.

Ammonium Oxalate Solution.—Dissolve 40 grams of ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, in hot distilled water and dilute to one liter.

Disodium Phosphate Solution.—Dissolve 100 grams of disodium phosphate ($Na_2HPO_4 \cdot 12H_2O$) in distilled water and dilute to one liter.

Starch Solution.—Dissolve 0.5 gram of soluble starch in 100 ml. of hot water. If soluble starch is not available, macerate 0.5 gram of ordinary starch to a creamy paste in a mortar with cold water, wash into 100 ml. of boiling water and boil for several minutes.

[19] Ref. J. C. Chiarino, C. A., **18**, 1799 (1924).

[20] Standard Method of the Solvay Process Company. By courtesy of the Company.

Allow to stand for a few minutes and then pour off the supernatant liquor for use. Starch Starch solutions do not keep well and for best results they should be prepared fresh every few weeks.

Sodium Thiosulfate Solution.—Dissolve 100 grams of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in distilled water and dilute to one liter.

Phenolphthalein.—Dissolve 3.5 grams of phenolphthalein in 650 ml. of grain alcohol and make up to 1000 ml. with distilled water.

Potassium Chromate Solution.—Dissolve 50 grams of neutral potassium chromate (K_2CrO_4) in 400 ml. of distilled water. Add enough silver nitrate to produce a slight red precipitate for the removal of chlorides. Filter and make up the filtrate to 1000 ml. with distilled water.

Methyl Orange.—Dissolve one gram of methyl orange in 1000 ml. of distilled water.

Potassium Sulfocyanate Solution.—Dissolve 50 grams of C. P. potassium sulfocyanate (KCNS) in distilled water and dilute to one liter.

Standard Solutions: *Tenth Normal Sulfuric Acid* (*N/10* H_2SO_4).—This solution should be prepared from a stock solution of normal sulfuric acid (N/H_2SO_4) by diluting exactly 100 ml. to 1000 ml. with distilled water.

The stock solution of normal sulfuric acid is prepared as follows:—This solution should contain 49 grams per liter of sulfuric acid (H_2SO_4) in distilled water. Mix 30 ml. of pure sulfuric acid of 1.84 specific gravity with 150 ml. of distilled water in a 1000 ml. measuring flask and allow to cool to room temperature. Dilute to 1000 ml. with distilled water and adjust the volume by titrating against 5.3 grams of chemically pure, dry sodium carbonate (Na_2CO_3) until 100 ml. of the acid will just neutralize the 5.3 grams of sodium carbonate, using methyl orange as an indicator.

A watch glass should cover the beaker while adding the acid to avoid mechanical loss. As the end-point is approached care should be taken to stir well, so that the color change from yellow to pink will be sharp and easily noticeable, the acid being added a drop at a time.

Tenth Normal Sodium Hydroxide (*N/10 NaOH*).—This solution should be prepared from a stock solution of normal sodium hydroxide (N/NaOH), by diluting exactly 100 ml. to 1000 ml. with distilled water.

The stock solution of normal sodium hydroxide is prepared as follows:—This solution should contain 40 grams per liter of sodium hydroxide (NaOH). Dissolve 41 grams of chemically pure sodium hydroxide in 250 ml. of distilled water in a 1000 ml. measuring flask. Allow to cool to room temperature and dilute to 1000 ml. Adjust by adding distilled water until 50 ml. are exactly neutralized by 50 ml. of normal sulfuric acid (N/H_2SO_4), titrating cold with 5 drops of phenolphthalein indicator.

Twentieth Normal Silver Nitrate (*N/20* $AgNO_3$).—This solution should contain 8.495 grams per liter of silver nitrate ($AgNO_3$). Dissolve 8.5 grams of chemically pure silver nitrate in distilled water to which one drop of colorless nitric acid (HNO_3) of 1.42 specific gravity has been added and dilute to 1000 ml. with distilled water. This solution is practically 1/20 normal. It may be standardized as follows:—Weigh out 0.8025 grams of chemically pure, dry, ammonium chloride (NH_4Cl). Dissolve in 250 ml. of distilled water and titrate 25 ml. of this solution with the silver nitrate solution, using 3 or 4 drops of potassium chromate (K_2CrO_4) solution as an indicator, until the red tint of the silver chromate just appears. If the silver nitrate solution is exactly N/20, 30.0 ml. will be consumed.

Tenth Normal Potassium Permanganate (*N/10* $KMnO_4$).—This solution should contain 3.16 grams per liter of chemically pure potassium permanganate ($KMnO_4$). Dissolve 3.2 grams of potassium permanganate crystals in 500 ml. of distilled water in a 1000 ml. measuring flask. Dilute to 1000 ml. Standardize as follows:—Add 0.67 grams of recrystallized, chemically pure sodium oxalate ($Na_2C_2O_4$) and about 150 ml. of distilled water to a liter boiling flask. Heat until dissolved, then add about 15 ml. of (1-3) sulfuric acid (H_2SO_4). Heat nearly to boiling and titrate with the potassium permanganate solution until a permanent pink color is obtained.

Adjust the solution to the required strength of calculate the proper factor from the following data:

100 ml. N/10 $KMnO_4$ solution = 0.67 grams of sodium oxalate.

The potassium permanganate solution should be kept in an amber colored or black painted bottle.

One Hundredth Normal Potassium Permanganate (N/100 $KMnO_4$).— Dilute exactly 100 ml. of the tenth normal potassium permanganate (N/10 $KMnO_4$) solution to one liter with distilled water. This solution should be kept in an amber colored or black painted bottle.

One Hundredth Normal Sodium Thiosulfate (N/100 $Na_2S_2O_3$).—This solution is made by diluting exactly 100 ml. of tenth normal sodium thiosulfate (N/10 $Na_2S_2O_3$(to 1000 ml. with distilled water.

Tenth normal sodium thiosulfate is prepared as follows:—Dissolve 24.83 grams of chemically pure sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in distilled water and dilute to one liter. Standardize as follows:—Place 40 ml. of tenth normal potassium permanganate (N/10 $KMnO_4$) solution in a 500 ml. flask, dilute to about 100 ml. with distilled water and add 15 ml. of)1-3(sulfuric acid (H_2SO_4), and 10 ml. of 10% potassium iodide (KI) solution (100 grams per liter). Titrate the liberated iodine with the tenth normal sodium thiosulfate solution until the color becomes a very light yellow. Then add about 0.5 ml. of fresh starch solution and complete the titration until the blue color just disappears. Adjust the volume of the solution from the following data:

40 ml. N/10 $KMnO_4$ = 40 ml. N/10 $Na_2S_2O_3$.

This solution should be standardized once a month.

Standard Iron Solution.—Dissolve 0.4911 grams of chemically pure, crystallized, ferrous ammonium sulfate ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) in 50 ml. of distilled water to which 20 ml. of (1-3) sulfuric acid (H_2SO_4) have been added. Warm the solution slightly and add tenth normal potassium permanganate (N/10 $KMnO_4$) until the iron is completely oxidized. Dilute the solution to 1000 ml.

1 ml. of this standard solution = 0.00007 grams Fe or = 0.0001 grams Fe_2O_3.

Methods of Analysis

Preparation of the Sample.—This operation should be carried out without unnecessary exposure to the air, as caustic soda readily takes up moisture and carbon dioxide, thus lowering the tests. A part of the sample to be tested is wrapped in a heavy cloth and crushed with a hammer, the remainder being saved for later determinations. Weighings should be made as quickly as possible.

Silica (SiO_2).—Dissolve 50 grams of the prepared sample in 200–300 ml. of distilled water in a 6-inch porcelain or Jena glass evaporating dish, add 2 drops of methyl orange and acidify cautiously with concentrated hydrochloric acid (HCl), avoiding loss by spattering. Evaporate to complete dryness on the steam bath, cover the dish and dehydrate the silica by heating in an oven at 110° C. for one hour. Cool, drench the residue with 10 ml. of concentrated hydrochloric acid, taking particular care that each particle of the residue is moistened with the acid. Then add 300 ml. of distilled water and warm on the steam bath to dissolve the soluble salts. Filter and wash the residue free from chlorides with cold water, adding only the first two washings to the filtrate. Transfer the filter paper and silica to a weighed platinum crucible, ignite in the open crucible over a low flame until the filter paper is burned off and then over the blast lamp for 10 minutes. Cool in a desiccator and weigh.

Weight of $SiO_2 \times 2 = \%$ SiO_2.

Iron and Aluminum Oxides ($Fe_2O_3 \cdot Al_2O_3$)—Dilute the filtrate from the determination of silica to 500 ml. in a measuring flask and mix thoroughly. Place 250 ml. of this solution in a 400 ml. beaker, add 1 ml. of nitric acid (HNO_3) and about 1 gram of ammonium chloride (NH_4Cl) and boil to oxidize the iron. Add slowly a slight excess of ammonium hydroxide (NH_4OH) and boil until the vapors have only a slight odor of ammonia. Allow the precipitate to settle, filter and wash the precipitate free from chlorides with hot water. Place the filter paper and precipitate in a weighed platinum crucible, carefully burn off the filter paper in the open crucible over a low flame and finally ignite with free access to the air for 10 minutes over the Meker burner or blast lamp. Cool in a desiccator and weigh.

Weight Fe_2O_3 & $Al_2O_3 \times 4 = \%$ Fe_2O_3 & Al_2O_3.

Iron Oxide (Fe_2O_3).—Transfer a 100 ml. aliquot portion of the 500 ml. filtrate from the determinations of silica to a 250-ml. beaker, add about 1 ml. of nitric acid (HNO_3) and boil to oxidize the iron. Then add a slight excess of ammonium hydroxide (NH_4OH) and continue boiling for a few minutes. Allow the precipitate to settle, filter and wash the precipitate about 5 times with hot water. Dissolve the precipitate off the filter in

about 20 ml. of (1-3) sulfuric acid (H_2SO_4) and wash into a 100 ml. graduated flask. Dilute to the 100 ml. mark and mix thoroughly. Pipette off 25 ml. of this solution into a 50 ml. Nessler tube, add 5 ml. of potassium sulfocyanate (KCNS) and dilute to the 50 ml. mark with distilled water.

To a second 50-ml. Nessler tube, add 5 ml. of (1-3) sulfuric acid and 5 ml. of potassium sulfocyanate, dilute nearly to the 50 ml. mark with distilled water and titrate with standard iron solution until the colors in the two Nessler tubes match.

Ml. Standard Iron Solution $\times 0.004 =$ % Fe_2O_3.

Aluminum Oxide (Al_2O_3).—% Fe_2O_3 & Al_2O_3—% Fe_2O_3 = % Al_2O_3.

Calcium Carbonate ($CaCO_3$).—Adjust the volume of the filtrate from the determination of iron and aluminum to about 300 ml. and acidify with (1-1) hydrochloric acid (HCl), adding about 5 ml. in excess. Add 10 ml. of ammonium oxalate solution, $(NH_4)_2C_2O_4$, heat to boiling, make slightly alkaline by adding ammonium hydroxide (NH_4OH) drop by drop and boil for a few minutes. Allow the mixture to stand in a warm place for 1–2 hours, filter and wash the precipitate free from chlorides with small quantities of hot water. Usually four or five washings suffice. Place the filter paper containing the precipitate in the beaker in which the precipitation was made and add 50 ml. of distilled water and 15 ml. of (1-3) sulfuric acid (H_2SO_4). Heat to 70–80° C. and titrate while hot under constant stirring with N/10 potassium permanganate ($KMnO_4$) solution until a faint, permanent pink color is obtained.

Ml. N/10 $KMnO_4 \times 0.02 =$ % $CaCO_3$.

Magnesium Carbonate ($MgCO_3$).—Acidify the filtrate from the determination of calcium with (1-1) hydrochloric acid (HCl), adding about 5 ml. in excess. Heat to boiling and add 10 ml. of disodium phosphate solution ($Na_2HPO_4 \cdot 12H_2O$). Then add ammonium hydroxide (NH_4OH) drop by drop under constant stirring until the solution becomes alkaline and a precipitate begins to form. If no precipitate forms the stirring should be continued for at least 5 minutes. Cool, add 30 ml. of strong ammonium hydroxide and stir for 5 minutes more if no precipitate forms. Allow the mixture to stand several hours or over night in a cool place. Filter and wash the precipitate with dilute ammonium hydroxide until the washings acidified with nitric acid (HNO_3) give no test for chlorides. Place the filter paper with the precipitate in an inverted position in a 250-ml. beaker and dry at 60–80° C. When quite dry and free from ammonia, add 25 ml. of distilled water and a measured excess of N/10 sulfuric acid (H_2SO_4). Stir until the paper is thoroughly disintegrated and titrate the excess of acid with N/10 sodium hydroxide (NaOH), using 2 drops of methyl orange as indicator.

Ml. N/10 H_2SO_4—ml. N/10 NaOH $\times 0.0169 =$ % $MgCO_3$.

Manganese (Mn).—Dissolve 40–50 grams of the sample in 300 ml. of distilled water, add 2 drops of methyl orange indicator, acidify with hydrochloric acid (HCl) and make slightly alkaline with ammonium hydroxide (NH_4OH). Pass hydrogen sulfide gas (H_2S) into the solution for ½ hour and allow the sample to stand at about 100° C. until the precipitate settles. Filter the precipitated sulfides and wash a few times with a weak solution of ammonium sulfide, $(NH_4)_2S$. Dry and ignite in a platinum crucible. To the residue in the crucible add 5–6 times its weight of sodium carbonate (Na_2CO_3), thoroughly mix and fuse over a burner.

Dissolve the fusion in 10 ml. of concentrated nitric acid (HNO_3) and heat for thirty minutes on the steam bath until all of the nitrous oxide fumes are expelled. Wash into a 250 ml. beaker with about 15 ml. of water, add 5 ml. of N/20 silver nitrate ($AgNO_3$) and warm to 70–80° C. Introduce 1 gram of ammonium persulfate $(NH_4)_2S_2O_8$, a little at a time, and shake until a good color is developed. Cool, shake, transfer to a 50 ml. Nessler tube and dilute to the 50 ml. mark. Should the color be too strong the solution must be diluted to 100 ml. and an aliquot portion used.

Compare the color with N/100 potassium permanganate ($KMnO_4$) titrated into 50 ml. of cold (1-4) nitric acid which has been previously boiled for several minutes to expel the nitrous oxide fumes. The (1-4) nitric acid is free from nitrous fumes and ready for use when it is colored by 1 drop of N/100 potassium permanganate.

$$\frac{\text{Ml. N/100 } KMnO_4 \times .011}{\text{Weight of Sample}} = \% \text{ Mn.}$$

Copper (Cu).—Dissolve 100 grams of sample in about 400 ml. of distilled water in a one liter beaker, and acidify slightly with (1-3) sulfuric acid (H_2SO_4). Bring the solution to a boil and add 20 ml. of strong sodium thiosulfate ($Na_2S_2O_3$) solution. Continue the boiling for ½ hour, filter, using suction and wash several times with hot water. Ignite

the filter paper in a porcelain crucible, dissolve the residue with 6 to 8 drops of concentrated nitric acid (HNO_3) and carefully evaporate to dryness over a low flame until all of the nitric acid is expelled. Dissolve the residue by heating gently with 10 ml. of N/10 sulfuric acid (H_2SO_4), wash into a 250 ml. Erlenmeyer flask and add a little sodium carbonate (Na_2CO_3) to precipitate basic copper carbonate. Acidify with acetic acid ($C_2H_4O_2$), cool and add from 2 to 5 grams of potassium iodide (KI) crystals. Titrate the liberated iodine with N/100 sodium thiosulfate ($Na_2S_2O_3$) until the color becomes light yellow. Then add about 0.5 ml. of freshly prepared starch solution and complete the titration with N/100 sodium thiosulfate until the blue color disappears.

$$\frac{\text{Ml. N/100 } Na_2S_2O_3 \times .063}{\text{Weight of Sample}} = \% \text{ Copper.}$$

ANALYSIS OF SODIUM CARBONATE

Soda Ash

Sodium carbonate, Na_2CO_3 (soda ash), and two forms with water of crystallization crystal carbonate, $Na_2CO_3 \cdot H_2O$, and soda crystals or washing soda, $Na_2CO_3 \cdot 10H_2O$, are commonly known. In the analysis of soda ash the customary demand is for total alkali, sodium carbonate, sodium bicarbonate, and sodium chloride. In a complete analysis, including the insoluble residue iron, Fe_2O_3, sodium sulfate, sodium thio-sulfate, sodium sulfite, sodium sulfide, sodium silicate, sodium hydroxide, alumina, and water may be required.

Procedure

Total Alkali, Na_2O.—Five grams of the soda ash are dissolved in 50 ml. of distilled water, preferably in an Erlenmeyer flask, with a funnel, the stem extending in the neck of the flask. 95 ml. of normal sulfuric acid are added and the solution boiled gently to expel the CO_2, the funnel prevents loss during boiling. After cooling, methyl orange indicator is added and the titration completed. The end-point is a faint pink color.

$$1 \text{ ml. N}/H_2SO_4 = .031 \text{ gram } Na_2O.$$

Note.—"New York and Liverpool test" the value of 1 ml. $N \cdot H_2SO_4 = .032$ g. Na_2O.

Sodium Bicarbonate, $NaHCO_3$.—Five grams of the soda ash are dissolved in 100 ml. of water and the solution titrated with normal sodium hydroxide until a drop of the solution on a spot plate produces an immediate dark color with a drop of silver nitrate.

$$1 \text{ ml. N/NaOH} = .084 \text{ gram } NaHCO_3.$$

Sodium Carbonate.—Deduct the ml. titration of NaOH for $NaHCO_3$ from the ml. H_2SO_4 titration for Na_2O, the difference in ml. multiplied by .053 = gram Na_2CO_3.

Sodium Chloride.—Two grams of the ash by the ammonia-soda process or 5 grams by the Leblanc process are dissolved in 50 to 100 ml. of distilled water and 5 ml. of colorless HNO_3 (sp.gr., 1.42) added. 2 ml. of ferric ammonium sulfate are used as indicator,[21] followed by a few drops of N/20 KCNS solution, the exact amount of this being noted. The chloride is now titrated with N/20

[21] *Ferric ammonium sulfate* 6% solution made by dissolving the salt in 50 parts of water to 6 parts of salt and adding an equal volume of colorless nitric acid.

$AgNO_3$ solution[22] until the color is just destroyed, then 1 ml. in excess is added. The precipitate is filtered off and washed. The filtrate and washings are now titrated with N/20 KCNS to a permanent pink color.[23]

The total ml. KCNS is deducted from the ml. $AgNO_3$ added and the difference multiplied by 0.002923 = gram NaCl.

NOTE.—See Volhard's method for chloride in Vol. I, page 271.

In addition to the above determinations the following may be desired:

Insoluble Matter.—Fifty grams of the soda ash are dissolved in about 500 ml. of water the insoluble matter allowed to settle, the clear solution decanted through a double filter, which has been weighed, and finally the residue washed onto the filter. The residue and filters are dried at 100° C. and weighed.

Weight minus tare of filters multiplied by 100 = per cent insoluble matter.

Iron, Alumina, Lime and Magnesia.—These are determined in the insoluble residue by dissolving out by means of dilute hydrochloric acid. The residue consists of *sand* and *carbonaceous matter*. Iron and alumina are precipitated out together by addition of ammonia according to the standard procedure, and determined as oxides, Fe_2O_3 and Al_2O_3. Iron may be determined in this residue by dissolving in HCl and titrating with stannous chloride according to the procedure given in Vol. I, page 373. Alumina is obtained by difference. Lime and magnesia will be found in the filtrates from iron and alumina precipitates. Calcium is thrown out as an oxalate and magnesium as a phosphate and determined as usual.

Sodium Sulfate.—Dissolve 5 to 10 grams in dilute HCl and add $BaCl_2$. The precipitate $BaSO_4$ is washed and ignited as usual.

$$BaSO_4 \times 0.6086 = \text{gram } Na_2SO_4.$$

Sodium Sulfite.—5 grams are dissolved in water and the solution acidified with acetic acid. Starch solution is added and the sulfite titrated with N/10 iodine until the blue color appears.

$$1 \text{ ml. N/10 I} = 0.006303 \text{ gram } Na_2SO_3.$$

Sodium Silicate.—Ten grams of the soda ash are treated with an excess of HCl and the solution evaporated to dryness, the silica dehydrated at 110° C. After leaching with water the insoluble SiO_2 is determined by filtering off and igniting by the standard procedure.

$$SiO_2 \times 2.0282 = Na_2SiO_3.$$

Sodium Sulfide.—This may be estimated by titration with an ammoniacal solution of silver nitrate (13.81 g. silver per liter = 1 ml. = .005 g. Na_2S). Add the reagent until no further precipitation occurs of Ag_2S. To get a good end-point the solution is filtered just before this point is reached and the titration completed. See also chapter on Sulfur, Volume I.

Loss on Ignition.—The sample 10 grams is ignited at a temperature slightly below 300° C. The loss is due largely to water and organic matter.

[22] N/20 silver nitrate contains 8.495 g. $AgNO_3$ per liter. Standardize against pure NaCl.

[23] N/20 potassium thiocyanate, KCNS, contains 4.86 grams of the salt per liter. The solution should be standardized against the silver nitrate solution.

MODIFIED SODAS

Causticized Ash

The determination of total alkali, sodium hydroxide and sodium carbonate are generally required. 20 grams of the sample are dissolved in water and the solution made to one liter. Aliquot portions of this solution are taken for analysis.

Total Alkali.—The determination is similar to that described for soda ash on page 2261, the test being made on 50 ml. of the solution equivalent to 1 gram of sample. It is advisable to add a slight excess of N/H_2SO_4 and titrate back with N/NaOH using methyl orange indicator. The end-point is a faint pink.

$$1 \text{ ml. } N/H_2SO_4 = 0.031 \text{ gram } Na_2O.$$

Sodium Hydroxide.—Fifty ml. of the sample equivalent to 1 gram of the solid is taken. The analysis is the same as that described for determining NaOH in caustic soda on page 2255.

Sodium Carbonate.—The difference between the acid titration for total alkali and that for sodium hydroxide is multiplied by 0.053 = gram Na_2CO_3.

Washing Soda (Neutral Soda)

The determination of total alkali, sodium carbonate, sodium bicarbonate, and sodium chloride are generally required. The method of analysis is the same as has been described under soda ash. See page 2261.

Methods for Testing Super Alkalies[24]

Preparation of Sample.—Weigh about 40 grams of the sample, using a weighing bottle and taking the weight of sample by difference. Wash into a standard 500 ml. graduated flask with distilled water, cool to room temperature, dilute to the mark and mix thoroughly. Use aliquot portions of this solution for the determinations.

All calculations below refer to the weight of this original sample

Total Alkali (Na_2O).—Titrate 25 ml. of the prepared solution in a 6 inch porcelain dish with $N/1$ H_2SO_4, using 3 drops of methyl orange as indicator.

$$\frac{\text{ml. } N/1\ H_2SO_4 \times 62.0}{\text{Wt. of original sample}} = \%\ Na_2O.$$

Sodium Hydroxide (NaOH).—To a 25 ml. aliquot of the prepared sample in a 6 inch porcelain dish, add about 100 ml. of $BaCl_2$ solution and titrate with N/1 HCl, using 5 or 6 drops of phenolphthalein as indicator, until the pink color is discharged.

$$\frac{\text{ml. } N/1\ HCl \times 80.02}{\text{Wt. of original sample}} = \%\ NaOH.$$

Sodium Carbonate (Na_2CO_3).—$(\%\ Na_2O - \%\ NaOH \times 0.7748) \times 1.7097 = \%\ Na_2CO_3$.

[24] The Solvay Process Company's Standard Method by courtesy of the Company.

Methods for Testing Neutral (Modified) Sodas

Total Alkali (Na_2O).—Weigh accurately 5 grams of the sample and dissolve in about 100 ml. of distilled water in a 250 ml. beaker. Titrate with N/1 H_2SO_4, using 3 drops of methyl orange as indicator.

$$\frac{\text{ml. N/1 } H_2SO_4 \times 3.1}{\text{Weight of sample}} = \%\ Na_2O.$$

Sodium Bicarbonate ($NaHCO_3$).—Place 8.4 grams of the sample in a 250-ml. beaker, dissolve in 50 ml. of distilled water and titrate with N/1 NaOH until a drop of the solution added to a drop of freshly prepared silver nitrate indicator on a spot plate gives instantly a dark color.

$$\frac{\text{ml. N/1 NaOH} \times 8.4}{\text{Weight of sample}} = \%\ NaHCO_3.$$

Sodium Carbonate (Na_2CO_3).—$(\%\ Na_2O - \%\ NaHCO_3 \times .3690) \times 1.7097 = \%\ Na_2CO_3$.

Sodium Chloride (NaCl).—Dissolve 5 grams of the sample in 50 ml. of distilled water in a 250-ml. beaker. Acidify slightly with iron indicator solution. Add a few drops of N/20 KCNS from a burette, noting the quantity; then titrate, while stirring constantly, with N/20 $AgNO_3$ to complete decolorization. Finally titrate back with N/20 KCNS until a faint reddish color persists.

$$\frac{(\text{ml. N/20 } AgNO_3 - \text{ml. N/20 KCNS}) \times .2923}{\text{Weight of sample}} = \%\ NaCl.$$

Moisture (H_2O).—$100\% - (\%Na_2CO_3 + \%NaHCO_3 + \%NaCl) = \%\ H_2O$. (By difference).

Analysis of Sodium Bicarbonate [25]

Place in a tared platinum crucible 4 g. of sodium bicarbonate and record the total weight. (Weight A.) Dry the sample in a desiccator for 24 hours over conc. H_2SO_4 and weigh. (Weight B.)

(1) $$\frac{(A-B) \times 100}{4} = \%\ \text{moisture.}$$

Heat the platinum crucible for about 2 or 3 hours in a muffle at temperatures between 500 and 600° F. Cool in a desiccator. (Weight C.)

(2) $$\frac{(B-C) \times 2.7097 \times 100}{4} = \%\ NaHCO_3.$$

[25] By courtesy of the Diamond Alkali Company through the kindness of J. D. Mattern.

Dissolve the contents of the platinum crucible in water and titrate with normal HCl using methyl orange as indicator.

$$\frac{\text{ml.} \times .053 \times 100}{4} = \%\ Na_2O \text{ expressed as } Na_2CO_3 \text{ as found in expression 2.}$$

$$\frac{\%\ \text{Bicarbonate} \times 84}{53} = \%\ \text{Bicarbonate expressed as } Na_2CO_3.$$

% total Na_2CO_3 minus % Na_2CO_3 from bicarbonate is equal to % Na_2CO_3 present in the sample.

Sodium Carbonate Determination in Sodium Hydroxide [26]

Commercial sodium hydroxide is now manufactured in a high degree of purity. The sodium carbonate contents may be found in some instances as low as .4%. In order to determine the exact amount of Na_2CO_3 present in the sample the common methods using 1 or 2 g. of sample cannot be applied because the difference in the two burette readings will be as little as .1 ml. (1/10 of 1 ml.).

Weigh out 220 g. of NaOH or if caustic liquor should be analyzed 440 g. of liquor, dissolve in H_2O and make volume up to 500 ml. Fill in a burette 50 ml. of this solution. Fill 500 ml. burette with normal HCl. Run out exactly 500 ml. into a liter beaker (lower mark of the burette). Add 300 ml. H_2O. Add 3 or 4 drops of methyl orange and titrate the acid with the NaOH solution in the 50 ml. burette until color changes to yellow. Note number of ml. of caustic used. Titration A. Place in another beaker exactly the same amount of caustic solution out of the same burette. Add 300 ml. 10% $BaCl_2$ solution and 3 or 4 drops phenolphthalein. Now titrate with normal HCl filled in the 500 ml. burette, until pink color just disappears. Titration B.

$$\frac{\text{Titration B} \times .04 \times 100}{22} = \%\ NaOH,$$

$$\frac{(A - B) \times .053 \times 100}{22} = \%\ Na_2CO_3.$$

Determination of Sodium Carbonate and Hydroxide in a Mixture. Winkler's Method

Principle.—A weighed portion of the sample is tested for total alkalinity with standard acid, using methyl orange indicator. A second weighed portion is treated with an excess of barium chloride reagent, which precipitates the carbonate leaving the hydroxide. This may now be titrated using phenolphthalein indicator. The reactions below show the steps of the procedure.

A. $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$. Methyl orange indicator.
$2NaOH + H_2SO_4 = Na_2SO_4 + H_2O$. Methyl orange indicator.

B. $Na_2CO_3 + BaCl_2 = BaCO_3 + 2NaCl$.
$2NaOH + BaCl_2 = Ba(OH)_2 + 2NaCl$.
$Ba(OH)_2 + H_2SO_4 = BaSO_4 + 2H_2O$. Phenolphthalein indicator.

[26] By courtesy of the Diamond Alkali Company through the kindness of J. D. Mattern.

Procedure.—Dissolve in a beaker 5–6 grams of the powder (carefully weighed) in water, transfer to a 500-ml. graduated volumetric flask, washing out the beaker into the flask. Make the solution to 500 ml. by diluting to the mark. For analysis take 100 ml. portion equivalent to 1/5 of the weight taken.

Portion A. To 100 ml. portion add methyl orange indicator and titrate with normal sulfuric acid until an orange red color is obtained. Record the ml. titration and mark as " A." This titration is due to the total Na_2CO_3 and NaOH.

Portion B. To 100 ml. portion 20–25 ml. of a 20% solution of $BaCl_2$. Add phenolphthalein indicator and titrate slowly with constant stirring with the normal acid, and record the ml. under " B." This is due to NaOH present in the sample.

Calculation—" A " is total alkalinity.
" A "–" B " is Na_2CO_3. Multiply ml. by 0.053.
" B " is NaOH. Multiply ml. by 0.04.

Notes.—Stirring is necessary in titration "B" since the acid must not be allowed to react with $BaCO_3$ as it would if there were an accumulation of the acid in one portion of the solution.

Total alkalinity may be determined by phenolphthalein by the following procedure. Titrate the solution in presence of this indicator. Now heat to boiling to expel CO_2, cool and again titrate. Repeat this as long as a color appears on boiling. When the solution remains colorless on boiling the end-point has been reached.

Estimation of the Carbonates and Hydroxides of Potassium and Sodium When together in Solution [27]

Procedure.—A measured volume of the solution is titrated, using phenolphthalein as indicator. The acid used is equivalent to all of the hydrate and half the carbonate; methyl orange is now added and the titration completed; the additional amount of the acid used is equivalent to half the carbonate, therefore the amount of acid required for the carbonates and for the hydrates can be calculated from these figures.

The fully neutralized solution is evaporated to dryness and the residue weighed. The result is the weight of the mixed sulfates, due to the carbonates and hydrates of potassium and soda in the solution.

Calculate the total acid required to its equivalent of potassium sulfate, subtract from this result the weight of the mixed sulfates, and the difference is due to the sodium sulfate in the mixed sulfates, owing to the difference in the molecular weights of potassium sulfate and sodium sulfate. The whole of the acid used has been calculated to potassium sulfate, and as the acid was neutralized by carbonates and hydrates, it is evident the proportion of total sulfate, due to the carbonates and hydrates, is equivalent to the amount of the acid used for each respectively; therefore the proportion of the above obtained difference due to the carbonates and the hydrates respectively is also proportional to the amount of acid used for each.

[27] W. A. Bradbury and F. Owen. Chem. News, **107**, 85, 2778 (1913).

Example.—A solution of the mixed carbonates and hydrates of potassium and sodium required:

(40 ml. NaOH : 40 ml. KOH) 80 ml. of acid to neutralize the hydrates.
(10 ml. Na_2CO_3 : 10 ml. K_2CO_3) 20 ml. of acid to neutralize the carbonates.
100 ml. total acid required to neutralize the solution.

Total acid 100 ml. calculated to K_2SO_4 $=0.87$ gram.

Total neutralized solution evaporated to dryness ($K_2SO_4+Na_2SO_4$) $=0.79$ gram.

Difference due to Na_2SO_4 in weighed sulfates $=0.08$ gram.

(K_2SO_4–Na_2SO_4) : Na_2SO_4 : : Diff. :
32 : 142 : : 0.08 : 0.355 Na_2SO_4 present in the mixed sulfates.

And the mixed sulfates 0.79 gram—0.355 = 0.435 K_2SO_4 present in the mixed sulfates.

Therefore the mixed sulfates consist of Na_2SO_4 0.355 gram, K_2SO_4 0.435 gram.

The proportion of the acid used for the hydrates is 80/100 and for the carbonates is 20/100.

Therefore the proportion of the difference (0.08) due to Na_2SO_4 from the hydrate NaOH is $0.08\times80/100=0.064$. For the carbonates $=0.08\times20/100=0.016$.

By the above ratios 32 : 142 : : 0.064 : 0.284 Na_2SO_4 from NaOH = 40 ml. N/10 acid. 32 : 142 : : 0.016 : 0.071 Na_2SO_4 from Na_2CO = 10 ml. acid.

80 ml. acid used for the hydrates $=0.696$ K_2SO_4.
0.284 Na_2SO_4 from the NaOH $=0.348$ K_2SO_4.
Difference = K_2SO_4 from KOH $=0.348=40$ ml. N/10 acid.
20 ml. acid used for the carbonates $=0.174$.
0.071 Na_2SO_4 from the Na_2CO_3 $=0.087$.
Difference = K_2SO_4 from K_2CO_3 $=0.087=10$ ml. acid.

The figures correspond with the quantities taken.

80 ml. of acid to neutralize the hydrates.

20 ml. of acid to neutralize the carbonates.

$Na_2SO_4=0.355$ { NaOH 0.284 = 40 ml. acid; Na_2CO_3 0.071 = 10 ml. acid } 80 ml. acid.

$K_2SO_4=0.435$ { KOH 0.348 = 40 ml. acid; K_2CO_3 0.087 = 10 ml. acid } 20 ml. acid.

Totals 0.790 0.790(a)100.

Calculate these sulfates to the corresponding hydrates and carbonates.

Optional Method for Determination of Sodium Bicarbonate and Sodium Carbonate in Presence of One Another

Five grams of the sample are dissolved in CO_2-free water, and the solution made up to exactly 250 ml. in a measuring flask. Aliquot portions of 25 ml.,

SODIUM HYDROXIDE SOLUTION AT 15°

LUNGE

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Per Cent Na_2O.	Per Cent NaOH.	1 Liter contains Grams	
					Na_2O.	NaOH.
1.007	1.0	1.4	0.47	0.61	4	6
1.014	2.0	2.8	0.93	1.20	9	12
1.022	3.1	4.4	1.55	2.00	16	21
1.029	4.1	5.8	2.10	2.70	22	28
1.036	5.1	7.2	2.60	3.35	27	35
1.045	6.2	9.0	3.10	4.00	32	42
1.052	7.2	10.4	3.60	4.64	38	49
1.060	8.2	12.0	4.10	5.29	43	56
1.067	9.1	13.4	4.55	5.87	49	63
1.075	10.1	15.0	5.08	6.55	55	70
1.083	11.1	16.6	5.67	7.31	61	79
1.091	12.1	18.2	6.20	8.00	68	87
1.100	13.2	20.0	6.73	8.68	74	95
1.108	14.1	21.6	7.30	9.42	81	104
1.116	15.1	23.2	7.80	10.06	87	112
1.125	16.1	25.0	8.50	10.97	96	123
1.134	17.1	26.8	9.18	11.84	104	134
1.142	18.0	28.4	9.80	12.64	112	144
1.152	19.1	30.4	10.50	13.55	121	156
1.162	20.2	32.4	11.14	14.37	129	167
1.171	21.2	34.2	11.73	15.13	137	177
1.180	22.1	36.0	12.33	15.91	146	183
1.190	23.1	38.0	13.00	16.77	155	200
1.200	24.2	40.0	13.70	17.67	164	212
1.210	25.2	42.0	14.40	18.58	174	225
1.220	26.1	44.0	15.18	19.58	185	239
1.231	27.2	46.2	15.96	20.59	196	253
1.241	28.2	48.2	16.76	21.42	208	266
1.252	29.2	50.4	17.55	22.64	220	283
1.263	30.2	52.6	18.35	23.67	232	299
1.274	31.2	54.8	19.23	24.81	245	316
1.285	32.2	57.0	20.00	25.80	257	332
1.297	33.2	59.4	20.80	26.83	270	348
1.308	34.1	61.6	21.55	27.80	282	364
1.320	35.2	64.0	22.35	28.83	295	381
1.332	36.1	66.4	23.20	29.93	309	399
1.345	37.2	69.0	24.20	31.22	326	420
1.357	38.1	71.4	25.17	32.47	342	441
1.370	39.2	74.0	26.12	33.69	359	462
1.383	40.2	76.6	27.10	34.96	375	483
1.397	41.2	79.4	28.10	36.25	392	506
1.410	42.2	82.0	29.05	37.47	410	528
1.424	43.2	84.8	30.08	38.80	428	553
1.438	44.2	87.6	31.00	39.99	446	575
1.453	45.2	90.6	32.10	41.41	466	602
1.468	46.2	93.6	33.20	42.83	487	629
1.483	47.2	96.6	34.40	44.38	510	658
1.498	48.2	99.6	35.70	46.15	535	691
1.514	49.2	102.8	36.90	47.60	559	721
1.530	50.2	106.0	38.00	49.02	581	750

AQUA AMMONIA

According to W. C. Ferguson

Degrees Baumé.	Sp. Gr. 60° F. / 60°	Per Cent NH_3.	Degrees Baumé.	Sp. Gr. 60° F. / 60°	Per Cent NH_3.	Degrees Baumé.	Sp. Gr. 60° F. / 60°	Per Cent NH_3.
10.00	1.0000	.00	16.50	.9556	11.18	23 00	.9150	23.52
10.25	.9982	.40	16.75	.9540	11.64	23.25	.9135	24.01
10.50	.9964	.80	17.00	.9524	12.10	23.50	.9121	24.50
10.75	.9947	1.21	17.25	.9508	12.56	23.75	.9106	24.99
11.00	.9929	1.62	17.50	.9492	13.02	24.00	.9091	25.48
11.25	.9912	2.04	17.75	.9475	13.49	24.25	.9076	25.97
11.50	.9894	2.46	18.00	.9459	13.96	24.50	.9061	26.46
11.75	.9876	2.88	18.25	.9444	14.43	24.75	.9047	26.95
12.00	.9859	3.30	18.50	.9428	14.90	25.00	.9032	27.44
12.25	.9842	3.73	18.75	.9412	15.37	25.25	.9018	27.93
12.50	.9825	4.16	19.00	.9396	15.84	25.50	.9003	28.42
12.75	.9807	4.59	19.25	.9380	16.32	25.75	.8989	28.91
13.00	.9790	5.02	19.50	.9365	16.80	26.00	.8974	29.40
13.25	.9773	5.45	19.75	.9349	17.28	26.25	.8960	29.89
13.50	.9756	5.88	20.00	.9333	17.76	26.50	.8946	30.38
13.75	.9739	6.31	20.25	.9318	18.24	26.75	.8931	30.87
14.00	.9722	6.74	20.50	.9302	18.72	27.00	.8917	31.36
14.25	.9705	7.17	20.75	.9287	19.20	27.25	8903	31.85
14.50	.9689	7.61	21.00	.9272	19.68	27.50	.8889	32.34
14.75	.9672	8.05	21.25	.9256	20.16	27.75	.8875	32.83
15.00	.9655	8.49	21.50	.9241	20.64	28.00	.8861	33.32
15.25	.9639	8.93	21.75	.9226	21.12	28.25	.8847	33.81
15.50	.9622	9.38	22.00	.9211	21.60	28.50	.8833	34.30
15.75	.9605	9.83	22.25	.9195	22.08	28.75	.8819	34 79
16.00	.9589	10.28	22.50	.9180	22.56	29.00	.8805	35.28
16.25	.9573	10.73	22.75	.9165	23.04			

ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonia solutions, varying with the temperature, correction must be applied according to the following table:

Corrections to be Added for Each Degree Below 60° F.			Corrections to be Subtracted for Each Degree Above 60° F.			
Degrees Baumé.	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14° Bé	.015° Bé	.017° Bé	.020° Bé	.022° Bé	.024° Bé	.026° Bé
16°	.021 "	.023 "	.026 "	.028 "	.030 "	.032 "
18°	.027 "	.029 "	.031 "	.033 "	035 "	.037 "
20°	.033 "	.036 "	.037 "	.038 "	.040 "	.042 "
22°	.039 "	.042 "	.043 "	.045 "	.047 "	
26°	.053 "	.057 "	.057 "	.059 "		

equivalent to 0.5 gram, are taken for analysis. The sample taken is titrated with N/5 hydrochloric acid in presence of phenolphthalein indicator (2–3 drops). The ml. titration recorded as " A," represents one half of the sodium carbonate present. Methyl orange indicator is now added (2–3 drops) and the titration with the acid continued until the solution turns faintly pink. The remaining carbonate and all of the bicarbonate are now titrated. The ml. titration is recorded as B.

$$2A \times 0.0106 = Na_2CO_3 \text{ and } B - A \times 0.0168 = NaHCO_3.$$

The author desires to acknowledge his indebtedness to Dr. W. B. Hicks, Chief of the Analytical Department, The Solvay Process Company, for his review of the section on Alkalies.

Determination of Small Amounts of Acid in Ether.—L. P. Hall, Ind. Eng. Chem., Anal. Ed., **2**, 244 (1930), recommends the use of sulfophthalein indicator such as bromothymol blue for the titration. Care should be exercised against CO_2 contamination. Color changes from green to blue.

ANALYSIS OF AQUA AMMONIA

Details for the complete analysis of crude ammoniacal liquor will be found in Volume I on pages 637–639.

The per cent ammonia in a solution free from other substances may be determined with a fair degree of accuracy by determining the specific gravity of the solution by means of the hydrometer. Since the specific gravity of aqua ammonia is less than 1, hydrometers graduated for measuring liquids lighter than water are used. The formula for 1 degree Baume = (140/sp.gr.) −130. Reference is made to the table on Aqua Ammonia.

Provided no other basic constituent is present, free ammonia in solution is best determined by direct titration with an acid in presence of methyl orange or methyl red as indicator.

Procedure.—About 10 grams of the solution in a weighing bottle with glass stopper is introduced into an 800-ml. Erlenmeyer flask containing about 200 ml. of water and sufficient $\frac{1}{2}$ normal sulfuric acid to combine with the ammonia and about 10 ml. in excess. The flask is stoppered and warmed gently. This forces out the stopper in the weighing bottle, the ammonia combining with the acid. Upon thorough mixing, the solution is cooled, and the excess of acid is titrated with half normal caustic.

$$\text{One ml. } \tfrac{1}{2}\ N \cdot H_2SO_4 = 0.0085 \text{ gram } NH_3.$$

$$\text{Factor. } H_2SO_4 \times 0.3473 = NH_3.$$

Note.—The aqua ammonia exposed to the air will lose ammonia, hence the sample should be kept stoppered. This loss of ammonia is quite appreciable in strong ammoniacal solutions.

Zinc Chloride Method for Determining Free Lime in Presence of Calcium Carbonate

The following procedure is of interest to the sugar chemist. The method developed by John C. Bailar, Great Western Sugar Company, depends upon

masking by means of a green dye the faint pink color produced by calcium carbonate in water on phenolphthalein. The color of the dye does not interfere in the titration of the alkalinity of calcium hydroxide. The cheapness of the procedure as compared with the iodine method commends its use in the commercial laboratory.

Solutions: ***Zinc Chloride Solution.***—This is made by dissolving 25 grams of the salt in a liter of water and filtering. 1 ml. of this solution is equivalent to about 0.01 g. CaO.

Sodium Hydroxide Solution.—The solution is made of such strength that 1 ml. is equivalent to 1 ml. of the zinc chloride solution

Indicator.—5 grams of phenolphthalein are dissolved in 500 ml. of 95% alcohol. This is mixed with a solution containing 2 grams of Alkali Fast Green E dissolved in 500 ml. of water.

Standardization.—The sodium hydroxide solution is standardized against a standard acid. The zinc chloride solution is now standardized against the alkali as follows: Into a liter flask containing 500 ml. of boiling hot distilled water 25 to 50 ml. of the NaOH solution are accurately measured from a burette. About 0.5–1.0 ml. of the indicator is added and the zinc chloride is run in until a green color is obtained that persists for half a minute. 10 ml. excess of the $ZnCl_2$ solution are now added and this excess, after vigorous shaking, is titrated with the NaOH solution until a lavender (not pink) color is obtained.

Determination.—In a dry one-liter flask is placed 1 gram of the sample. 500 ml. of boiling, CO_2-free water are added. As soon as the lime has hydrated, the solution is titrated with zinc chloride solution until a green color appears, an excess of zinc chloride is added and the excess determined with standard NaOH solution as in case of the standardization above. The end-point is a lavender color.

Notes.—The flask used with the lime determination must be dry, otherwise the water in small amount reacting with the sample will cause difficulty in the subsequent procedure.

The quantity of indicator in standardization and the determination must be the same, as the quantity influences results. The Alkali Fast Green E dye is made by the National Aniline Company, Buffalo, N. Y.

ANALYSIS OF ALKALINE MIXTURES

Sodium Carbonate, -Bicarbonate, -Borate *

The determination of sodium carbonate, sodium borate and sodium bicarbonate in solids or in solution together with neutral salts can be carried out by titration with standard acid and alkali.

Sampling.—In all determinations in which mixtures of carbonate and bicarbonate are evolved the contact of the sample with the air or moisture must be avoided as far as possible. Solutions of carbonate and bicarbonate will be altered rapidly until an equilibrium is established, which is independent of the initial composition of the sample.

* Courtesy of H. H. Chesny.

In the case of solids weigh out 0.5 to 2.0 g. and make up with carbon dioxide free water to 100 ml. Weigh out a second sample for the bicarbonate determination.

In the case of liquid samples the dilution of 10 ml. to 100 ml. is convenient. The bicarbonate determination requires an undiluted sample; it is convenient to use 2 or 5 ml.

Procedure.—Total Alkali: Titrate a sample with 0.1 normal hydrochloric acid, using as little methyl orange indicator as possible, to the dead neutral point.

Let " *a* " = ml. of 0.1 n HCl used.

Borax: Use the same sample which has been titrated with the hydrochloric acid to the dead neutral point in the titration for total alkali, boil for 2 or 3 minutes, cool sufficiently, preferably below 20° C., add mannitol[28] (3 g. for each gram of $Na_2B_4O_7$) or cerelose (30 g. for each gram borate), followed by phenolphthalein indicator (excess not harmful) and titrate with 0.1 normal sodium hydroxide solution until a pink color is obtained. Add more of the polyhydroxy compound and, if a fading of the pink color occurs, continue the titration with the sodium hydroxide solution until on addition of mannitol or cerelose no more fading takes place.

Let " *b* " = ml. of 0.1 n NaOH used.

Bicarbonate: The separate samples (as described under " sampling ") are used for this determination. The samples are placed in a *dry* flask and at once an excess of 0.1 normal sodium hydroxide solution is added, the solution shaken gently for a few seconds (shaking violently too long will result in absorption of carbon dioxide from the air) followed by a slight excess of neutral barium chloride solution.

Let " *c* " = ml. of 0.1 n NaOH added.

The solution together with the white precipitate (consisting of barium carbonate (and sulfate)), is titrated with 0.1 normal hydrochloric acid using phenolphthalein as indicator until colorless.

Let " *d* " = ml. of 0.1 n HCl used.

Determine the carbonate content of the sodium hydroxide solution by measuring out 100.0 ml., adding barium chloride and phenolphthalein indicator and titrating with 0.1 n HCl.

Let "*e*" = ml. of 0.1n HCl used.

Calculation:

Total alkali Na_2O: " *a* " times 0.0031 = g. of Na_2O in sample taken.

Bicarbonate $NaHCO_3$: [(" *c* " + " *e* "/100) − (" *d* " − $\frac{1}{2}$ " *b* ") × 0.0084] = g. of sodium bicarbonate in sample taken. *Note:* The actual weights of the original sample used for the titration on total alkali and borax[29] must be equal

[28] Mannitol as well as cerelose should be tested for neutrality.

[29] In the presence of large amounts of borax the precipitate is filtered off and washed carefully with CO_2-free water.

to the weight of the undiluted sample taken for the bicarbonate determination, or due allowance for the ration between the number of ml. used in "*a*," "*b*," "*c*" and "*d*" must be made, if a different weight is taken.

Borax $Na_2B_4O_7 \cdot 10H_2O$: "*b*" times 0.00955 = g. of sodium tetraborate decahydrate, or "*b*" times 0.00505 = g. of anhydrous sodium tetraborate in sample taken.

For more accurate analysis:

$$[(\text{"}b\text{"} \times \text{"}e\text{"}/100) + \{\text{"}b\text{"} \times 0.02(100 - \text{"}e\text{"})\}]$$

times the above given factors equals the grams of borax.

Sodium carbonate Na_2CO_3: $\text{"}a\text{"} - [(\text{"}c\text{"} \times \text{"}e\text{"}/100) - (\text{"}d\text{"} - \text{"}b\text{"})] \times 0.0053$ = g. of sodium carbonate in sample taken.

DETERMINATION OF pH BY THE COLORIMETRIC METHOD[1]

Introductory

Acidity and alkalinity have long been recognized as important factors in practically all branches of research and industrial work. Sugar manufacturers and refiners, electroplaters and electrotypers, paper manufacturers, sanitary engineers, agriculturists, bacteriologists, biologists, pathologists, etc., have therefore used various methods for detecting and controlling acidity and alkalinity, since they have learned by experience that this factor has a very marked effect on the yield and quality of their products, the efficiency of manufacturing processes, corrosion of metals, adsorption of dyes by fabrics and clays, the stability of various materials, the growth of bacteria, the diagnosis of diseases, etc.

The colorimetric method of measuring hydrogen ions has many advantages that appeal to practical workers. It is rapid and simple in operation and compared to other methods very inexpensive. The entire pH range or any portion of it can be covered by means of portable equipment for use in factory or field. The difficulties are such as can invariably be remedied. For these reasons the colorimetric method is now being used for investigation and control in every field where the determination of hydrogen ions is important.

By mutual agreement the hydrogen electrode is regarded as the fundamental standard in all determinations of hydrogen ion. All other methods are secondary whether potentiometric (quinhydrone electrode, glass electrode, antimony electrode) or colorimetric. All such methods must be standardized against the hydrogen electrode.

Meaning of pH

Intensity of heat is expressed as degrees on the thermometer scale, and density as degrees on the Baume scale. Similarly the pH scale is used to denote intensity of acidity and alkalinity.

The numbers from 0 to 14 are used to express pH values, that is, intensity of acidity and alkalinity. The value pH 7.0, halfway between 0 and 14, is the neutral point; that is, a solution having a pH of 7.0 is neither acid nor alkaline. The numbers below 7.0 denote acidity, intensity of acidity *increasing* as the numbers *decrease*. Thus a solution of pH 6.4 is very slightly acid, one of pH 6.0 is more intensely acid and one of 4.6 is still more intensely acid, etc.

On the other hand the numbers between 7.0 and 14.0 are used to denote alkalinity, the intensity of alkalinity *increasing* as the numbers *increase*. Thus a solution of pH 7.2 is very slightly alkaline, one of pH 8.6 is more intensely alkaline and one of 10.4 is still more intensely alkaline. These numbers represent absolutely definite degrees of acidity and alkalinity and therefore a state-

[1] Chapter by W. A. Taylor and F. R. Mc Crumb, W. A. Taylor & Co.

ment such as "acidify to pH 5.6" or "make alkaline to pH 9.4" has a very definite meaning which cannot be expressed by the terms "slightly acid or alkaline."

The values used in the pH scale are derived in the following manner. If N/10 solutions of the three acids, hydrochloric, acetic and boric are titrated under suitable conditions it is found that the total acidity is the same in all cases. It is apparent, however, that these three acids differ radically in properties. Hydrochloric acid is a powerful acid whereas acetic and boric are relatively weak. Bases also show differences even when the total neutralizing ability is the same. Solutions of sodium bicarbonate, sodium carbonate and sodium hydroxide are entirely different even when the strengths are such that they will neutralize the same amount of acid per unit volume. These facts have been known for years but it was not until the ionization theory was developed that they could be explained.

The theory of ionization holds that certain types of chemical compounds are split apart or dissociated in aqueous solution, yielding electrically charged particles known as ions. These ions are responsible for many of the properties of aqueous solutions. One general property is conduction of electric current. When acids are dissociated they produce hydrogen ions and negative ions, $HA \leftrightarrows H^+ + A^-$, and the acidic nature is determined by the extent to which such dissociation occurs, acidity being due to the hydrogen ions. Strictly speaking free H ions probably do not exist in aqueous solution as such but probably combine with water to form H_3O^+. Practically this does not affect our assumptions. The differences among the three acids named above are due to the concentration or activity of hydrogen ions which they produce. In 0.1 N solutions these are roughly in the proportions hydrochloric 15,000, acetic 200, boric 1.

In a similar way bases produce hydroxyl ions, $BOH \leftrightarrows B^+ + OH^-$, and the basic nature of an alkaline solution is determined by the extent to which such dissociation occurs, alkalinity being due to the hydroxyl ions. For example the ratios of the concentrations of hydroxyl ions in 0.1 N solutions of sodium hydroxide, sodium carbonate and sodium bicarbonate are roughly 16,667 : 667 : 1.

The fundamental reaction between acids and bases in aqueous solutions is between hydrogen and hydroxyl ions to produce water, thus $H^+ + OH^- \leftrightarrows HOH$-$(H_2O)$. Since pure water conducts a current to a very small degree this reaction must be slightly reversible, i.e. even in pure water some hydrogen and hydroxyl ions must exist. However this ionization is extremely slight only 1 molecule of water in about 555,000,000 being dissociated. Using the symbols for concentration, hydrogen ions $[H^+]$, hydroxyl ions $[OH^-]$ and undissociated water $[H_2O]$, according to the law of chemical mass action, the product of $[H^+]$ and $[OH^-]$ divided by $[H_2O]$ is constant, i.e. $\frac{[H^+][OH^-]}{[H_2O]} = K$. Since $[H_2O]$ is extremely large as compared to $[H^+]$ and $[OH^-]$, it can be regarded as constant and $[H^+]\,[OH^-] = Kw$, the ionization product of water, which at any definite temperature is a constant. This constant, Kw, has been determined by a variety of methods and found to be approximately 1/100,000,000,000,000 or $1/10^{14}$ or 10^{-14} at 25° C. The use of exponents such as 10^{-14} enables one to readily handle extremely large or small numbers. This can be easily under-

stood by recalling that $10\times10\times10$ is the same as 10^3 and $\frac{1}{10}\times\frac{1}{10}\times\frac{1}{10}$ is the same as $\frac{1}{10^3}$. By using a negative exponent simple fractional terms can be dispensed with, i.e. $\frac{1}{10^3}=10^{-3}$, etc.

Since in pure water the H ion and OH ion concentrations must be the same, if $[H^+]\,[OH^-]=10^{-14}$ then $[H^+]=[OH^-]=10^{-7}$. A solution in which $[H^+]=[OH^-]=10^{-7}$ is neutral. Whenever $[H^+]$ is geater than $[OH^-]$ that is greater than 10^{-7} at 25° C., the solution is acid; whenever $[H^+]$ is smaller than $[OH^-]$ that is smaller than 10^{-7} at 25° C. the solution is alkaline. From the equation $[H^+]\,[OH^-]=Kw$ it is seen that a simple relation always exists between $[H^+]$ and $[OH^-]$, thus $[H^+]=\frac{Kw}{[OH^-]}$. It is therefore unnecessary to refer to OH ion concentration at all and the term hydrogen ion concentration is used even when referring to very alkaline solutions such as N sodium hydroxide, which contain a vanishingly small number of hydrogen ions, the predominating ion being the hydroxyl ion.

Expressing hydrogen ion concentrations as 1/10,000,000 or even as 10^{-7} is extremely inconvenient. For this and other reasons, such as plotting curves, etc., Sorensen introduced the method of expressing such values in terms of the negative logarithm to the base 10. He called this the hydrogen exponent and gave it the symbol pH. Thus pH is the negative logarithm of the hydrogen ion concentration or the logarithm of the reciprocal of the hydrogen ion concentration, i.e. $pH=-\log[H^+]=\log\frac{1}{[H^+]}$, and $[H^+]=10^{-pH}$. Accordingly if in a neutral solution $[H^+]=10^{-7}$, the pH will be 7.0. Similarly pOH is the logarithm of the reciprocal of the hydroxyl ion concentration, $pOH=\log\frac{1}{[OH^-]}$ and pKw is the logarithm of $\frac{1}{Kw}$. If $Kw=10^{-14}$, $pKw=14$. The relationship between hydrogen and hydroxyl ion is shown by recalling that if $[H^+]\,[OH^-]=Kw=10^{-14}$, then $pH+pOH=pKw=14$, and $pH=14-pOH$. So in pure water $pH=pOH=7.0$. In 0.01N HCl where $[H^+]=10^{-2}$, $pH=2.0$. In 0.01N NaOH where $[OH^-]=10^{-2}$, $pOH=2.0$ and $pH=14-2=12.0$.

The use of pH (negative logarithm) sometimes causes confusion at first. It should always be remembered that a decrease in pH denotes an increase in active acidity and an increase in pH denotes a decrease in active acidity (increase in active alkalinity). In addition since pH is a logarithmic function, a solution having pH 6.0 contains 10 times as many hydrogen ions as one with pH 7.0. Similarly a solution with pH 5.0 contains 100 times and a solution with pH 4.0, 1000 times as many hydrogen ions as one with pH 7.0.

A simple way to deal with hydrogen ion concentration is in terms of normality. If an acid solution contains 1 g. of available (ionizable) hydrogen per liter it is said to be normal. Similarly a solution can be said to be normal with respect to hydrogen ions when it contains 1 g. of ionized hydrogen per liter. Since $\frac{1}{[H^+]}$ is the reciprocal of the normality of hydrogen ions, pH can be defined

as the logarithm of the denominator expressing such normality. Thus when $[H^+] = \frac{N}{100}$, pH = log 100 = 2.0. When $[H^+] = \frac{N}{10{,}000}$, pH = log 10,000 = 4.0, etc. The relationship between pH and hydrogen ion concentration is shown in the table below. Expressing $[H^+]$ both as decimal fractions and as 10 with negative exponents shows how pH is derived.

H-Ion Concentration		pH
1.0	10^{0}	0.0
0.1	10^{-1}	1.0
0.01	10^{-2}	2.0
0.001	10^{-3}	3.0
0.000,1	10^{-4}	4.0
0.000,01	10^{-5}	5.0
0.000,001	10^{-6}	6.0
0.000,000,1	10^{-7}	7.0
0.000,000,01	10^{-8}	8.0
0.000,000,001	10^{-9}	9.0
0.000,000,000,1	10^{-10}	10.0
0.000,000,000,01	10^{-11}	11.0
0.000,000,000,001	10^{-12}	12.0
0.000,000,000,000,1	10^{-13}	13.0
0.000,000,000,000,01	10^{-14}	14.0

Several concrete examples may serve to make clear the exact meaning of pH. Although a N/10 solution of hydrochloric acid contains 3.65 g. of HCl and 0.1 g. of ionizable hydrogen per liter, only 84.0% (18° C.) is ionized (active). Recent developments in the theory of ionization indicate that strong acids are completely ionized and that the degree of ionization ordinarily assumed is only apparent being due to interionic forces. Therefore the normality with respect to ionized hydrogen is not N/10 but $\frac{0.84N}{10}$ or $\frac{N}{11.90}$. Then pH = log 11.90 = 1.08.

A N/10 solution of acetic acid contains the same amount of ionizable hydrogen as does N/10 HCl namely 0.1 g. but only 1.3% (18° C.) is ionized. The normality with respect to ionized hydrogen is only $\frac{0.013\ N}{10}$ or $\frac{N}{769}$ and pH is log 769 = 2.89.

The apparent degree of dissociation of N/10 NaOH is 92.9% at 25° C. The normality with respect to OH ions is therefore $\frac{0.929\ N}{10} = \frac{N}{10.76}$ and pOH is log 10.76 or 1.03. pH = 14 − 1.03 = 12.97.

Dissociation in $\frac{N}{10}$ ammonium hydroxide proceeds only to the extent of 1.33% at 25° C. Normality with respect to OH ions is therefore only $\frac{0.0133\ N}{10}$ or $\frac{N}{752}$ and pOH = 2.88. pH = 14 − 2.88 = 11.12.

When certain salts are dissolved in water not only does ionization occur but there is a tendency to react with the water as BA + HOH ⇆ HA + BOH. With salts of strong acids and strong bases such as sodium chloride this tendency is zero and such salts do not affect the pH of water. With salts of strong acids and weak bases such as aluminum sulfate, ferric chloride, etc. the strong acid

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resulting dominates the weak base and the solution is acid. The reaction for aluminum sulfate is $Al_2(SO_4)_3+3H_2O \leftrightarrows 3H_2SO_4+Al(OH)_3$. With salts of weak acids and strong bases, the strong base resulting dominates the weak acid and the solution is alkaline. The reaction for sodium carbonate is $Na_2CO_3+2H_2O \leftrightarrows H_2CO_3+2NaOH$. This general reaction is termed hydrolysis and salts subject to it are for practical purposes either acids or bases.

Buffer Action

In the case of a solution of a single pure acid or alkali, if the concentration and degree of ionization (real or apparent) are known, the pH can be calculated as shown above. In actual practice such a situation will rarely arise. Invariably solutions contain more than one substance. Frequently some of these substances form what is known as a buffer system and serve to modify and stabilize the pH.

When 1 ml. of 0.01 N HCl is added to 1 liter of pure water of pH 7.0, the pH will drop to about pH 5.0. If however the same amount of acid were added to a solution containing a mixture of KH_2PO_4 and Na_2HPO_4 of pH 7.0 the drop in pH would be very small. This is illustrated by the curves on page 2279. The phosphate mixture has the ability to resist change in pH on addition of acid or alkali. It has what is called buffer action and such a mixture constitutes a buffer system or mixture. Such action is encountered in numerous solutions found in nature and in industrial processes. All mixtures of weak acids and their salts or of weak bases and their salts are buffer mixtures. Some of the most common buffer mixtures are acetic acid-acetate, carbonic acid (CO_2)-bicarbonate, citric acid-citrate, mixed phosphates, etc. Other common buffering substances are proteins (gelatine, casein, etc.).

The mechanism of buffer action is most easily shown by means of the acetic acid acetate system. In a solution of acetic acid dissociation occurs only to a small extent as follows, $HAc \leftrightarrows H^+ + Ac^-$. Sodium acetate however dissociates practically completely, $NaAc \leftrightarrows Na^+ + Ac^-$ and yields a large number of acetate ions $[Ac^-]$. A N/10 solution of acetic acid has pH 2.89 but a solution N/10 with respect to both acetic acid and sodium acetate has pH 4.63. The pH has been increased i.e. the H ion concentration has been lowered. The question arises as to what has become of the H ions. The mass law equation for acetic acid is $\frac{[H^+]\,[Ac^-]}{[HAc]} = Ka$, where Ka is the ionization constant. If any one of the three concentrations be changed there must be a change in the others else Ka could not remain constant. In the case just cited the acetate ion concentration $[Ac^-]$ has been enormously increased so the H ion concentration $[H^+]$ has to decrease. The unionized acetic acid will automatically become greater so practically what occurs is that more inactive (unionized) acetic acid is formed removing H ions from the solution. In this system the concentrations of acetate ion $[Ac^-]$ and unionized acetic acid [HAc] are always extremely large compared to the concentration of H ions $[H^+]$ so that the ratio $\frac{[Ac^-]}{[HAc]}$ partially determines the reaction or pH. This is important when dilution is necessary.

If small amounts of a strong acid (hydrochloric) be added to the system, the large concentration of acetate ions quickly converts most of the H ions added to

unionized acetic acid and $[H^+]$ increases only slightly. If a base (sodium hydroxide) is added H ions are neutralized but more acetic acid is ionized producing additional H ions to take the place of those neutralized and $[H^+]$ decreases only slightly. Of course any buffer system has its limits and large amounts of acid or base will overcome the buffer capacity. Each buffer system has a rather narrow pH zone over which it functions. However, by using different systems i.e. different mixtures, practically the entire pH range can be covered. This is extremely advantageous since it is possible to prepare solutions of constant pH which serve as standards and it also serves as a means of holding an industrial solution close to the optimum pH. In the case of fairly concentrated solutions of strong acids and bases, since the concentration of unionized substance is relatively small, there is no reserve supply of H or OH ions. However there is such a large concentration of H or OH ions that for practical purposes such systems function as buffer systems. For example when the concentration of either N/10 HCl or N/10 NaOH is reduced to N/100, the pH is changed only about 1 unit.

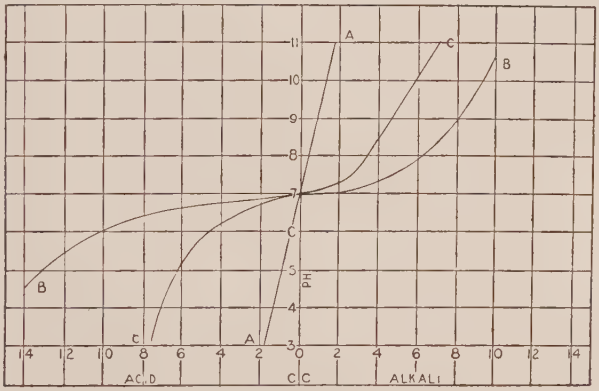

FIG. 311.

The stability of any buffer system will depend on total concentration, and the ratio of salt to weak acid or base. Reasonable changes in concentration will not materially change the pH as long as the ratio remains the same. In the acetate system the ratio $\frac{[Ac^-]}{[HAc]}$ does not change on moderate dilution and the change in pH when the system N/10 acetic acid–N/10 sodium acetate is diluted twenty fold is less than 0.1 pH. Many solutions met with in practice are buffered. This is an advantage since colorimetric pH measurements can be made on such solutions even when highly colored or turbid by diluting with distilled water. The degree of dilution possible depends on the concentration and the specific buffer system but the safest procedure is to dilute only as far as necessary to make satisfactory readings.

Buffer action can be illustrated graphically by means of titration curves (Fig. 311). Three such curves are shown in which various amounts of M/5 HCl and M/5 NaOH are added to 100 ml. samples of (A) distilled water, (B)

a buffer mixture composed of KH_2PO_4 and Na_2HPO_4 in which the total concentration is approximately 0.1 M, and (C) a similar buffer mixture in which the total concentration is one half of B, all samples having an initial pH of 7.0. The abscissa show the amounts of acid or alkali added and the ordinates show the pH of the respective mixtures.

The extremely steep curve (A) for distilled water shows that this substance is devoid of buffer action since small amounts of acid or alkali change the pH markedly. In the pronouncedly acid and alkaline ranges the curve flattens out because one is then dealing with relatively concentrated solutions of the strong acid and base, where pH varies only moderately with concentration.

The curve (B) for the 0.1 M phosphate mixture differs radically from (A). Addition of 11 ml. of acid only changes the pH from 7.0 to 5.8, whereas the addition of 6 ml. of alkali only changes the pH from 7.0 to 7.8. Beyond these points the change becomes more pronounced. Between 5.8 and 7.8 the curve is relatively flat and in this zone the phosphate mixture shows strong buffer action. As the curve indicates, buffer action is strongest near the middle of the relatively flat portion. It actually reaches a maximum at about 6.8 where the concentrations of KH_2PO_4 and Na_2HPO_4 are the same, i.e. $\frac{[Na_2HPO_4]}{[KH_2PO_4]} = 1$. The steepness of the curve above and below the zone 5.8–7.8 indicates little resistance to change in pH.

Curve (C) resembles (B) in contour but the relatively flat portion or zone of effective buffer action is much shorter, extending only from about 6.5 to 7.5. This shows the effect of concentration on buffer action.

These curves show that not all buffer mixtures have the same buffer capacity. Van Slyke (J. Biol. Chem., **52**, 525 (1922)) has formulated a method of expressing the differences in terms of buffer capacity. A solution has a buffer capacity of 1 when the reaction of a liter of it is changed one pH unit upon the addition of one equivalent of acid or base. A knowledge of the buffer capacity of a solution is frequently of considerable value since it indicates how easily the optimum pH may be maintained in practice, and also what precautions are necessary in determining the pH. It also provides a practical method of determining the amount of acid or alkali required to adjust the pH.

The requirements for buffer action should be clearly kept in mind. Mere presence of salts does not ensure buffer action. Salts of strong acids and strong bases impart no buffer action to a solution. Solutions which contain only salts of weak acids and weak bases may not be buffered. To ensure buffer action a buffer system must be present i.e. both salt and weak acid or weak base and the pH of the solution must be within the effective zone of the particular system.

Tables showing the method of preparation for various buffer mixtures can be found in Clark; The Determination of Hydrogen Ions, 1928, Williams and Wilkins, Baltimore, Md.

The following table gives some common buffer systems and the approximate pH of maximum buffer capacity. The zone of effective buffer action will vary with concentration but the general average will be ± 1.0 pH from the value given, for concentrations approximately 0.1 molar.

Glycocoll-sodium chloride-hydrochloric acid	2.0
Potassium acid phthalate-hydrochloric acid	2.8
Primary potassium citrate	3.7
Acetic acid-sodium acetate	4.6
Potassium Acid Phthalate-Sodium Hydroxide	5.0
Secondary Sodium Citrate	5.0
Carbonic Acid-Bicarbonate	6.5
Primary Phosphate-Secondary Phosphate	6.8
Primary Phosphate-Sodium Hydroxide	6.8
Boric Acid-Borax	8.5
Borax	9.2
Boric Acid-Sodium Hydroxide	9.2
Bicarbonate-Carbonate	10.2
Secondary Phosphate-Sodium Hydroxide	11.5

The Use of Indicators

For making pH determinations substances known as indicators are required. An indicator is a substance that gives different colors or different shades of color at different pH values. Thus, phenol red changes from yellow at pH 6.8 to a deep red at pH 8.4; that is, if phenol red is added to a solution having a pH of 6.8 it will give this solution a yellow color. If added to another solution of pH 7.0 it will give a somewhat redder shade of yellow. If added to other solutions having pH values of 7.2, 7.4, 7.6, etc. the amount of red color imparted to the solution will increase progressively until at pH 8.4 the solution will have a deep red color. Therefore if phenol red is added to any solution having a pH value between 6.8 and 8.4, the pH of that solution is determined by observing the color obtained. The method for accurately reading the pH value is explained later in this section.

Phenol red covers only a limited part of the pH scale but other indicators are available for other parts. Thus bromcresol green covers the range pH 3.8–5.4 and its color change is from yellow at pH 3.8 to blue at pH 5.4. Thymol blue covers the range pH 8.0–9.6 and its color change is from yellow at pH 8.0 to blue at pH 9.6. A complete list of indicators which cover the pH scale 0.2 to 13.6, with their pH ranges and color changes, is given in the table.

Name	pH Range	Color Change
Acid cresol red	0.2– 1.8	Red-yellow
Acid meta cresol purple	1.2– 2.8	Red-yellow
Thymol blue	1.2– 2.8	Red-yellow
Benzo yellow	2.4– 4.0	Red-yellow
Bromphenol blue	3.0– 4.6	Yellow-blue
Bromcresol green	3.8– 5.4	Yellow-blue
Methyl red	4.4– 6.0	Red-yellow
Chlorphenol red	5.2– 6.8	Yellow-red
Bromcresol purple	5.2– 6.8	Yellow-purple
Bromthymol blue	6.0– 7.6	Yellow-blue
Phenol red	6.8– 8.4	Yellow-red
Cresol red	7.2– 8.8	Yellow-red
Meta cresol purple	7.6– 9.2	Yellow-purple
Thymol blue	8.0– 9.6	Yellow-blue
Phthalein red	8.6–10.2	Yellow-red
Tolyl red	10.0–11.6	Red-yellow
Parazo orange	11.0–12.6	Yellow-orange
Acyl blue	12.0–13.6	Red-blue

Indicators are weak acids or bases in which the ionized form differs in constitution and color from the normal form. An indicator acid will dissociate as $HIn \leftrightarrows H^+ + In^-$, HIn being the acid form and In^- the alkaline form. The mass law expression will be $\frac{[H^+]\,[In^-]}{[HIn]} = K_I$. Then $\frac{[In^-]}{[HIn]} = \frac{K_I}{[H^+]}$. Since K_I is a constant the ratio $\frac{[In^-]}{[HIn]}$ will depend on the value of $[H^+]$, the hydrogen ion concentration. This ratio determines the color that the indicator will show. For example with phenol red the acid form [HIn] is yellow and the alkaline form $[In^-]$ is red, consequently as $[In^-]$ increases the color changes from yellow through orange to red. When HIn is half transformed $[HIn] = [In^-]$ and so $[H^+] = K_I$. When the hydrogen ion concentration is the same as the ionization constant of the indicator, the concentrations of the acid and alkaline forms of the indicator are equal. The value of K_I varies for different indicators and determines the range of hydrogen ion concentration over which each indicator functions. If $[H^+] = K_I$ then $pH = pK_I$, where $pK_I = \log \frac{1}{K_I}$. While this determines the theoretical midpoint of the pH range of each indicator, the actual range used in practice depends on how readily the colors can be distinguished by the eye. Consequently the practical range is determined experimentally. While pK_I is a function of pH, it is also affected to some extent by other factors, such as salt concentration, proteins and temperature.

A satisfactory indicator for practical pH work must have certain well defined qualifications. It must give well-defined color changes over a relatively short range; it must not be unduly affected by substances other than hydrogen or hydroxyl ions; it must immediately give colors that are stable for a reasonable length of time, so that there will be no errors due to changes taking place during the determination; its solution must be a stable reagent. An indicator that fades rapidly, precipitates, undergoes change in color due to the presence of salts, colloidal materials, etc., attains a stable color slowly, or is unstable as a reagent, is certain to prove objectionable in practice.

The essential requirements in applying the colorimetric method for the determination of pH are (1) An accurately prepared solution of indicator, (2) a set of color standards prepared from measured amounts of buffer solutions having accurately adjusted pH values and containing accurately measured amounts of the indicator solution. Standards in intervals of 0.2 pH are usually employed. Such a set for phenol red will consist of standards with the pH values 6.8, 7.0, 7.2, 7.4, 7.6, 7.8, 8.0, 8.2 and 8.4. These standards can be placed in test tubes or ampoules having uniform bores. Ampoules are more satisfactory since they can be sealed. If a measured volume of clear sample is treated with the same amount of indicator as is present in the standards, the resulting color will depend on the pII of the sample and by comparing this color with the color standards the pH can be determined. It is essential that all measurements be accurate and that the bore of the color standards and test tube used for the sample be practically the same. The intensity of color and depth of liquid in both cases should be uniform.

If the materials being tested are *absolutely* clear and colorless accurate determinations can be made by comparing the color of the test sample with those of

the color standards, as outlined above. Most solutions encountered in actual practice are however somewhat turbid or colored or both. Therefore when an indicator solution is added to such a material the resulting color will not match with the color standards which contain none of the color or turbidity of the sample. For this reason some sort of comparator is required. In fact all determinations should be made with a comparator since the presence of even minute quantities of color or turbidity may cause considerable error or even prevent a match all together when an attempt is made to match the sample directly with the color standards. The procedure employed in all comparators is essentially the same so the Slide Comparator (see page 2283) will be used to illustrate the principle.

In making a determination three of the test tubes are filled to the mark (5 ml.) with the material to be tested and 0.5 ml. of the indicator solution is added to the middle tube. The color standards are then moved back and forth in front of the test sample, always making sure that, when a comparison is made, one of the ampoules of distilled water is in front of the middle test tube containing the indicator. Two consecutive color standards will then be directly in front of the two tubes of test sample containing no indicator. The arrangement of the three tubes of test sample, the two color standards and the ampoule of distilled water is illustrated in figure 312 below.

AA, BB, CC represent the three slots in the base and any three corresponding slots in the color standard slide. If we consider the color standards as consisting of distilled water and indicator only, which is permissible since they contain no turbidity and no color except that given them by the indicator, it is clear that on looking through slots AA, BB, and CC, one is looking through exactly the same materials—sample, indicator, distilled water—in each case. This arrangement therefore eliminates any effect of color or turbidity in the sample so that, when the proper color standards are in place, the color of the sample will match one of the color standards or lie between the colors of two consecutive standards.

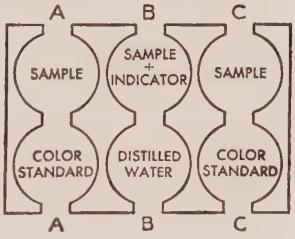

Fig. 312.

Readings should never be made by matching against either end standard in a given set. Thus a sample may match the bromthymol blue color standard marked pH 6.0 and actually have a pH value of 5.0, 4.2, etc. If a match with the standard marked 6.0 is obtained the determination should be repeated using an indicator covering a lower part of the pH scale, for example, chlorphenol red (pH 5.2–6.8), bromcresol green (pH 3.8–5.4), etc., until a match is obtained with a standard other than the end one. Similarly if a sample matches the bromthymol blue standard marked 7.6, the test should be repeated using phenol red (pH 6.8–8.4) or a higher indicator if necessary.

The table on page 2281 shows that the ranges of the various indicators overlap. Thus the values pH 6.0–6.8 are common to both chlorphenol red and bromthymol blue, the values pH 6.8–7.6 are common to both bromthymol blue and phenol red, etc. It is therefore usually possible to make a test on any given sample with two different indicators and thus check results. This is one of the outstanding advantages of using several indicators to cover a wide pH range

instead of a single wide range indicator, such as the so called universal or utility indicators. With the single test wide range indicator there is no way of checking results and marked errors may be made with no means of detecting them.

Colorimetric Determination of Buffered Materials

One of the most important factors to be considered when the colorimetric method is applied is the degree to which the material being tested is buffered. This is especially important when the pH of colored and turbid materials must be determined. When a highly colored or turbid sample is buffered it can frequently be diluted with distilled water to a point where satisfactory readings can be made with the comparator method without introducing appreciable error. For example, sewage sludges have been accurately tested when a dilution of 1 : 49 was necessary.[2] The presence of buffer systems in the sludge makes this possible.

In applying the dilution procedure to any substance it is advisable to continue the dilution beyond that required for satisfactory readings so as to determine the point at which marked change starts to take place. This will furnish information on the buffer capacity of the substance being tested. In all cases the distilled water used should be of excellent quality and it should have a pH of 6.4 to 6.8.

It is usually advisable to employ dilution and make the tests on the supernatant liquid after any solids have partially settled. Filtration should be avoided unless it is definitely known that changes in pH will not result. During filtration there may be a gain or loss in carbon dioxide or an action by the filtering medium (paper, glass wool, etc.) which will introduce errors.

Unbuffered or Slightly Buffered Materials

Some materials encountered in practice are not very highly buffered and a few are unbuffered. In such cases care must be exercised in determining the pH since such solutions are very susceptible to change. Among such materials are most waters, soil extracts, paper extracts, white water, pure sugar liquors, flotation feeds, laundry rinses, clay filtrates, etc.

Distilled water is devoid of buffer action and special precautions must be observed in testing it. Absolutely pure water has pH 7.0 at 25° C. Ordinary distilled water is usually acid, due to absorption of carbon dioxide. Distilled water in equilibrium with the carbon dioxide of the air will have pH 5.7. It may be supersaturated with carbon dioxide to give a pH as low as 5.0. Carbon dioxide may be removed by boiling in Pyrex vessels to give water with a pH of 6.6 to 6.8 but superpure water with pH 7.0 can best be secured by means of a special still. Distilled water should always be kept in Pyrex or tinned vessels and contact with air held at a minimum. In making aqueous solutions or extractions of slightly buffered materials, proportions of material and water should be held constant so that results on different samples will be comparable.

In determining the pH of buffered solutions reasonable differences between the pH of the sample and the indicator solution will not affect the results.

[2] McCrumb, Sewage Works Journal, **1**, 534 (1929).

However, in the case of unbuffered solutions the pH of the indicator solution must be fairly close to the pH of the sample or the indicator will change the pH (Acree and Fawcett, Ind. Eng. Chem. Anal. Ed., **2**, 78 (1930)). For this reason the pH of the indicator solution should always be at or near its own midpoint. For example bromcresol green, 4.8, bromthymol blue, 6.8, cresol red, 8.0, etc. This is why it is impossible to secure accurate results on slightly buffered materials when a single wide range indicator (universal, utility, etc.) is employed. It has been shown that errors as high as 3.0 pH may result (McCrumb, Ind. Eng. Chem. Anal. Ed., **3**, 233 (1931)). This is because the pH of the wide range indicator may vary so much from that of the sample.

Where extremely accurate results are desired on unbuffered materials, it may be advisable to use several solutions of the same indicator adjusted to different points on its range, such as bromthymol blue at 6.2, 6.8, 7.4. If the unknown is devoid of buffer action as in the case of distilled water, for example, three values may result such as 6.6, 6.8, and 7.0 respectively. Since the reading 6.8 coincides with the pH of the indicator solution used for that test, the actual pH is 6.8.

All indicator solutions should be adjusted to their respective midpoints and kept in Pyrex bottles sealed with rubber stoppers. Soft glass bottles and cork stoppers should never be used or marked changes in pH may occur. Indicator solutions should not be unduly exposed to the air (poor seals, etc.) since carbon dioxide may lower the pH. In case changes occur the pH can be again adjusted by adding dilute (N/10) acid or alkali as required comparing the indicator solution in a special pair of tubes with the appropriate standard. If, however, buffered solutions are being tested, only gross changes in the pH of indicator solutions need be considered.

In making a pH determination on a slightly buffered solution the indicator solution should be placed in the test tube and the solution being tested run in from a pipette holding the tip of the pipette near the bottom of the tube. Mixing is then secured by stirring either with the tip of the pipette or with a thin glass rod. Mixing should never be done by placing finger or thumb over the mouth of the tube. The recommended procedure prevents introduction of impurities such as carbon dioxide, etc. and gives accurate results. This is really the only way unbuffered materials can be tested since electrometric methods are not reliable on very slightly buffered solutions.

The Effect of Salts

As stated previously the color of any indicator may be influenced by the actual salt concentration as well as the pH. This effect is commonly known as the "salt error."

By varying the concentration of a buffer mixture and determining the pH both by a hydrogen electrode and the colorimetric method it will be found that absolute agreement occurs only at the concentration of buffer employed in making the standard. Above this concentration the colorimetric method will give results that are slightly higher than those secured by the hydrogen electrode and below this concentration the colorimetric results will be slightly lower. This is illustrated by the results given in the following table.

Effect of Varying the Concentration of a Buffer Mixture

Molar Conc.	Hydrogen Electrode pH	Colorimetric pH	Difference pH Hyd. Elect. −pH Color.
0.200	6.33	6.40	−0.07
0.100	6.42	6.45	−0.03
0.050	6.50	6.50	0.00
0.020	6.57	6.55	+0.02
0.010	6.62	6.55	+0.07
0.005	6.68	6.55	+0.13

It will be noted that absolute agreement occurs only at a molar concentration of 0.05, the one employed in making the color standards. Of course none of the difference are pronounced.

The effect of sodium chloride is shown by the data in the following table secured by adding variable amounts of sodium chloride to a phosphate buffer mixture having the same concentration as was employed in the preparation of the color standards.

Effect of Sodium Chloride

Sodium Chloride Molar Conc.	Hydrogen Electrode pH	Colorimetric pH	Difference pH Hyd. Elect. −pH Color.
0.00	6.40	6.40	0.00
0.05	6.25	6.40	−0.15
0.10	6.23	6.40	−0.17
0.20	6.15	6.35	−0.20
0.50	6.00	6.25	−0.25
1.00	5.90	6.15	−0.25

Similar data secured by adding magnesium chloride to the same phosphate buffer mixture show the influence of a divalent salt.

Effect of Magnesium Chloride

Magnesium Chloride Molar Conc.	Hydrogen Electrode pH	Colorimetric pH	Difference pH Hyd. Elect. −pH Color.
0.00	6.40	6.40	0.00
0.05	5.70	5.90	−0.20
0.10	5.40	5.80	−0.40
0.20	5.20	5.65	−0.45
0.50	4.70	5.26	−0.56

The indicators used in making the colorimetric measurements given in the three tables above were bromthymol blue, chlorphenol red, para nitrophenol, and bromcresol green.

Additional information on salt effect can be secured by consulting Clark,[3] Kolthoff,[4] Guntelberg and Schiodt,[5] Sendroy and Hastings,[6] McCrumb and Kenny,[7] and Blum and Bekkedahl.[8] The last paper deals exclusively with nickel electroplating and electrotyping solutions.

The investigations of Guntelberg and Schiodt and Hastings and Sendroy would indicate that in the case of the indicators bromphenol blue, bromcresol green, bromcresol purple and phenol red, when the effects of salts are correlated with ionic strengths, salts of different valence types show at the same ionic strengths approximately like effects on the apparent dissociation constants of the indicators.

The ionic strength of a solution is obtained by multiplying the concentration of each ion by the square of that ion's valence number, summing these products and dividing by two. In general the buffer solutions used as standards in the colorimetric method have ionic strengths of 0.05 to 0.1.

In the majority of cases the differences encountered in industrial practice may have little significance. The correction can be determined and applied for each case but frequently it can be disregarded. For example in the case of a nickel plating bath it may make little difference to the plater whether the bath is controlled at pH 5.8 colorimetrically or 5.4 electrometrically. However, to avoid confusion when comparing procedures, the method employed should be given.

The Effect of Proteins

Systematic calibration when proteins are encountered will prove to be much more difficult than in the case of salts. Salts are at least substances of a definite nature, whereas the term protein is used in a very loose manner. For this reason so-called "protein errors" of indicators should never be applied unless it is known definitely that these variations were determined on solutions that are practically identical with the one being tested.

For example many "protein errors" have been determined on materials like beef broth or some type of bacteriological media. On many of these materials the proteins have undergone considerable hydrolysis, or they are rather dilute. Anyone taking the variations so determined and using them in the measurement of the pH, of say gelatine or casein, might quickly get into trouble.

The following table shows some variations encountered on a 1% solution of gelatine to which variable amounts of sulfuric acid and sodium hydroxide had been added. The gelatine was ash free with a pH of 4.80 (isoelectric). Sulfuric acid was used because this acid is most likely to be encountered in practice.

[3] Clark, "The Determination of Hydrogen Ions," 1928, Williams and Wilkins.
[4] Kolthoff, "The Colorimetric and Potentiometric Determination of pH," 1931, John Wiley and Sons, Inc.
[5] Guntelberg and Schiodt, Z. Physik Chem., **135**, 393 (1928).
[6] Sendroy and Hastings, J. Biol. Chem., **82**, 200 (1929).
[7] McCrumb and Kenny, J. Soc. Chem. Ind., **49**, 425T, 427T (1930).
[8] Blum and Bekkedahl, Trans. Electro Chem. Soc., **56**, 291 (1929).

Effect of Gelatine

Hydrogen Electrode pH	Colorimetric pH	Difference pH Hyd. Elect. −pH Color.	Indicator
2.48	2.40	0.08	Meta cresol purple
2.79	3.20	−0.41	Benzo yellow
3.19	3.55	−0.36	Benzo yellow
3.51	3.85	−0.34	Bromcresol green
3.65	4.00	−0.35	Bromcresol green
3.88	4.20	−0.32	Bromcresol green
4.47	4.60	−0.13	Bromcresol green
4.80	4.85	−0.05	Bromcresol green
5.07	5.00	0.07	Bromcresol green
6.16	6.20	−0.04	Chlorphenol red
6.59	6.65	−0.06	Bromthymol blue
6.80	7.20	−0.40	Phenol red
7.39	7.90	−0.51	Phenol red—Cresol red
7.78	8.50	−0.72	Thymol blue

It will be noted that the differences encountered near the isoelectric point are insignificant being within the sensitivity of the colorimetric method employed. When hydrochloric acid is used the differences are greater in the acid range.

The variations between pH measurements by the hydrogen electrode and the colorimetric method in the precipitation of casein by hydrochloric acid have been determined by Clark and others [9] using methyl red; and by Miss Benton [10] using bromcresol green.

Effect of Temperature

Since the pH of a solution depends on the degree of ionization of its constituents and this may be affected by temperature, the influence of temperature on pH is an important factor. Irrespective of the method of measurement employed determinations must be made at a fixed temperature. In the majority of cases a temperature of 25° C. is the most satisfactory although variations in temperature from 20° C. to 30° C. are usually insignificant for practical purposes.

Certain buffer systems are more sensitive to temperature variations than others. This is particularly true of the borate and carbonate series. Solutions which depend on a carbonate equilibrium are always susceptible to changes in temperature.

In the case of nickel solutions not only does the pH change with temperature but the color of the solution itself may change. Consequently the blanks used in the comparator method should be at the same temperature as the sample to which indicator has been added.

The sulfonephthalein indicators are not influenced by temperature changes to a marked degree but methyl orange and indicators resembling methyl orange are very susceptible to such changes. The indicators LaMotte Yellow, Hellige Orange and Benzo Yellow belong to this class.

[9] Clark, Zoller, Dahlberg and Weimar, Ind. Eng. Chem., **12**, 1163 (1920).
[10] Benton, Ind. Eng. Chem., **20**, 15 (1928).

Specific Effects

In the case of certain sulfonephthaleins the shade of color depends on concentration and depth of layer. Dichromatism is most noticeable in practice with such indicators as bromphenol blue and bromcresol purple. The transmitted light in such cases is primarily red and blue and the ratio of red and blue will vary with the depth of layer. In testing turbid solutions much of the light is reflected by the particles and this gives the same effect as a thin layer of liquid and this tends to modify the color. In such cases it is advisable to substitute another indicator.

Off color, while not exactly common to all indicators may occur in the case of most two color indicators under certain conditions. Suspensions, emulsions and solutions of a colloidal nature may cause this difficulty. Concentrated solutions of such salts as zinc chloride and sulfate frequently give off colors with the sulfonephthaleins. Sometimes on standing a precipitate, presumably of basic salts, will settle out and the colors then secured on the supernatant liquid may then correspond with the color standards. In such cases the original solution may appear clear to the eye, but it must contain dispersed solids which cause the off color of the indicator. When dealing with such solutions the nitrophenols may be used. When tubes and standards are observed through a blue glass satisfactory color distinctions can usually be secured.

The nitrophenols ordinarily employed for this purpose are 2.4 Dinitrophenol (Alpha) (pH 2.8–4.4), 2.5 Dinitrophenol (Gamma) (pH 4.2–5.8), para nitrophenol (pH 5.4–7.0) and meta nitrophenol (pH 7.2–8.8). The color changes are all from practically colorless to varying shades of yellow.

For further details Michaelis and Gyemant [11] should be consulted.

Difficulty is sometimes encountered in testing soap solutions. In fairly dilute solutions the results may be in good agreement with the hydrogen electrode but certain indicators tend to give low results as the concentration of soap is increased. This is particularly true of thymol blue.

Some indicators are apparently influenced by certain ions in some way not as yet explainable. Alizarine Yellow G (pH 10.0–12.0), Alizarine Yellow R, (pH 10.0–12.0), nitro yellow (pH 10.0–11.6) tend to give high results in the presence of calcium salts.

Michaelis [12] has demonstrated the precipitation of bromthymol blue in a solution of quinine hydrochloride.

However, not all the sulfonephthaleins are precipitated by quinine as Michaelis appears to think. Chlorphenol red gives satisfactory readings in such cases. None of the nitrophenols are precipitated by quinine. Precipitation of bromthymol blue also takes place in solutions used as local anaesthetics in dentistry.

There are a few rare instances in which bromthymol blue gives results that are slightly lower than those found by other sulfonephthaleins. This has been pointed out by Sharp and McInerney [13] in the testing of milk.

[11] Michaelis and Gyemant, Biochem. Z., **109**, 165 (1920) (see Clark, "The Determination of Hydrogen Ions," 1928, p. 128).

[12] Michaelis, "Practical Physical and Colloid Chemistry," Trans. by Parsons, 1925, p. 41.

[13] Sharp and McInerney, J. Biol. Chem., **70**, 729 (1926).

Similar results are sometimes encountered in testing concentrated solutions of sulfonated oils.

Effect of Chlorine

The action of chlorine must sometimes be taken into consideration in water treatment plants, paper mills, textile mills, etc., whenever the dosage of chlorine is high enough to affect the indicators. When such action occurs the results secured are influenced by the particular indicators in use, the concentration of indicator employed, the buffer capacity of the solution being tested, the temperature and, of course, the concentration of available chlorine.

In the procedure employed with the Slide Comparator (Fig. 313) the danger point with the sulfonephthaleins is about 2.0 parts per million of active chlorine. Whenever lower concentrations of indicator are employed as in Nessler tubes, etc., the action of chlorine may cause errors at lower concentrations of chlorine.

There appears to be two types of reaction, chlorination and oxidation. In the case of chlorphenol red and phenol red chlorination appears to predominate at first and the chlorinated dyes which result have lower pH ranges than the original dyes. This results in an increase in the alkaline color which leads to results that are higher than they should be. Of course on longer standing if the concentration of chlorine is high enough fading will occur due to destruction of the dye by oxidation. In the case of the other sulfonephthalein dyes the action is largely destructive and the readings tend to be low or off colors are secured.

The nitrophenols are more stable in the presence of active chlorine and can sometimes be used when the concentration of chlorine is as high as 200 parts per million.[14]

One disadvantage of the nitrophenols should be pointed out here. They are all fairly acidic and their solutions are difficult to stabilize at any definite pH. Consequently they are more liable to give erroneous results in testing unbuffered samples than are the sulfonephthaleins.

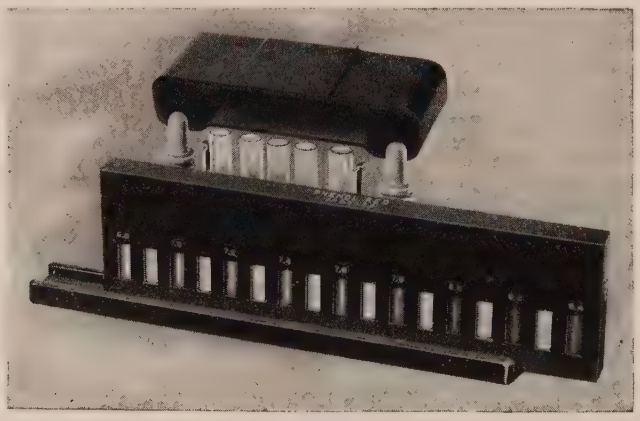

Fig. 313.

[14] Lewis and Kukolich, Paper Trade Journal, **95**, No. 11, p. 28 (Sept. 15, 1932).

Colorimetric pH Equipment

Colorimetric pH equipment can be made by the worker if desired using buffer mixtures in test tubes or ampoules but it is more satisfactory to purchase such equipment. Several types are available and the outstanding ones will now be described in some detail. Fuller descriptions can be secured from the manufacturers.

The Taylor Slide Comparator

The Slide Comparator consists of two principal parts, the slide and the base, as shown in the cut below. The Slide is a Bakelite case 10 inches long, 2¾ inches high and ⅝ inch thick. It contains 17 vertical holes and 17 horizontal slots which pass through the exact centers of the holes. In these holes are placed the 9 color standards for any given indicator and 8 ampoules of distilled water, the color standards alternating with the ampoules of distilled water. All these ampoules are held in place by a lid which is screwed on the top of the slide.

The base consists of two parts. The lower part contains a slot for the slide fitted with a key to stop the slide at the end standards, two holes containing vials of indicator solution, with 0.5 ml. pipettes and nipples, five holes containing test tubes, and a closed compartment for a ground glass plate. Horizontal slots run through the three central holes in the base holding the test tubes, these slots corresponding exactly with any three of the slots in the slide. The upper part of the base serves as a cover for the vials and test tubes when the set is not in use. It is fastened to the lower part by means of spring catches. The complete set, including the slide, is 10 inches long, 2⅛ inches wide and 4 inches high, and weighs only 2 pounds.

Making a pH determination consists in only three simple operations.

1. After removing the top of the base, three of the test tubes are placed in the holes back of the slots in the base and filled to the mark (5 ml.) with the sample to be tested.

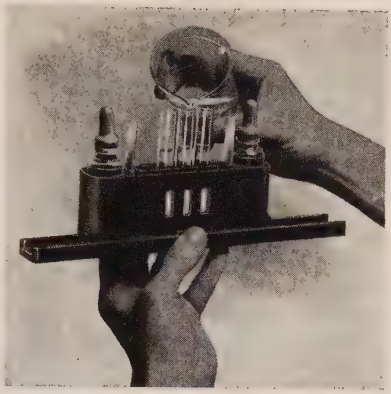

Fig. 314.

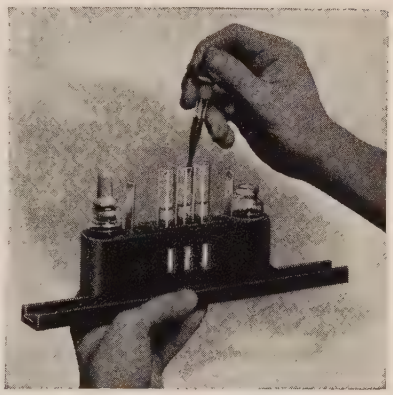

Fig. 315.

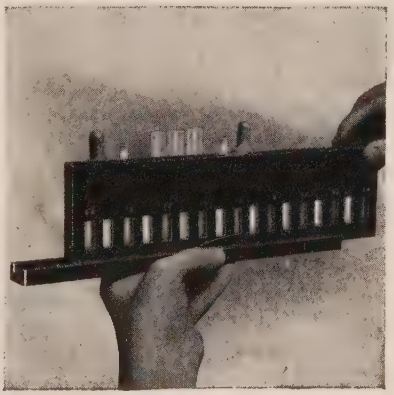

Fig. 316.

2. To the central tube 0.5 ml. of the indicator solution is added, by means of the pipette and nipple, and the contents are thoroughly mixed.

3. The slide containing the color standards is now placed in position on the base and, holding the instrument toward a window or other source of daylight, the slide is moved back and forth in front of the test samples until a color match is obtained. The pH is then read off directly from the values on the front of the slide.

Since all color standard slides are interchangeable, that is they can be used with one base, the range of a single slide Comparator can be increased by purchasing additional slides and a supply of the corresponding indicator solutions, with pipettes and nipples. For ranges longer than that of one indicator, however, the Long Range and Dalite Slide Comparators are recommended.

All color standards provided for the various models of slide comparators are guaranteed to retain their accuracy for a period of five years.

The Long Range Slide Comparator

This set is designed to meet the needs of workers who require a portable set covering a wider range. It is made in six models covering the range of any 3, 4, 5, 6, 7, or 8 indicators respectively between the limits pH 0.2 and pH 13.6. It is flexible since its range can be increased simply by securing additional color standard slides.

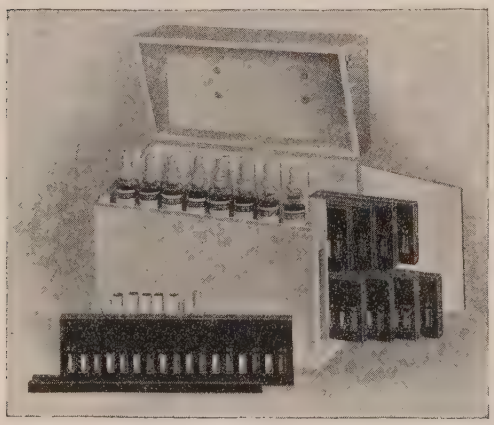

Fig. 317.

Each Long Range Slide Comparator contains one complete Slide Comparator; 2 to 7 extra color standard slides; vials of the corresponding indicator solutions, with 0.5 ml. pipettes and nipples; and 14–5 ml. test tubes. All models are contained in a polished wooden case 11½ inches long, 9 inches high and 5¾ inches wide, with a handle for carrying. All equipment necessary for making tests is contained in the case so that these sets can be used in field, laboratory or plant. The total weight of the set varies from 7½ lbs. to 9½ lbs. depending on the number of slides.

The method for making determinations is exactly the same as that described for the single Slide Comparator.

Dalite Slide Comparator

In many cases it is necessary to make pH determinations at night. Also in many plants even during the day time the light is not suitable for this type of work. The use of ordinary electric light bulbs and even the so-called dalite bulbs is not satisfactory. The Dalite Slide Comparator enables the worker not only to make determinations at night with just as great accuracy as during the day but also assures him that measurements made at night will check those made on the same materials by ordinary daylight.

The set is made in 6 models to cover the range of any 3, 4, 5, 6, 7 or 8 indicators respectively between the limits of pH 0.2 and pH 13.6 in intervals of 0.2 pH. The set is flexible since its range can be increased simply by purchasing additional color standard slides and vials of the corresponding indicator solution.

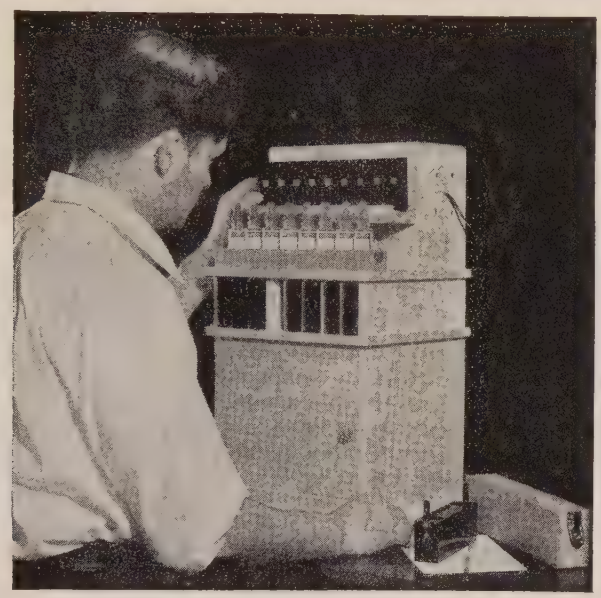

Fig. 318.

The pH equipment supplied with this set consists of one complete Slide Comparator; any 2 to 7 additional color standard slides; vials of the corresponding indicator solutions with pipettes and nipples; and 10–5 ml. test tubes. Each slide contains 9 color standards for any given indicator and these slides fit in slots in the front of the case as shown in the illustration. Each vial of indicator solution is placed directly above the corresponding color standard slide, thus eliminating error due to the use of the wrong indicator solutions. A top protects the vials when the set is not in use.

The comparator base is supported by a shelf on the front of the box. Directly behind the slots in the base is a piece of Dalite glass and in the compartment behind this is a special 25 watt electric light bulb, with cord, switch and socket. In the lower part of the box is a cupboard of sufficient size to hold four 1000 ml. Pyrex bottles. This cupboard serves not only as storage for stock bottles of indicator solution but also to bring the comparator to a convenient height for making readings. A rack on the inside of the door holds 10–5 ml. test tubes. A test tube brush is also supplied with the set.

In making determinations three of the 5 ml. test tubes are filled to the mark with the solution to be tested, the proper color standard slide is placed on the base and 0.5 ml. of the corresponding indicator solution is added to the middle tube by means of the pipette and nipple. The light is then turned on and the

slide is moved back and forth until a match is obtained with one of the color standards. The pH value is then read off directly from the values on the slide.

The Roulette Comparator

The Roulette Comparator consists essentially of a stationary base and metal band, and a wooden drum which revolves inside the metal band, on ball bearings. A block, which contains three slots, and which is drilled to hold three graduated test tubes, is fastened to the front of the metal band. A 40 watt lamp is fixed in the center of the base and is connected with a standard plug by means of a lamp cord, a piece of Dalite glass is placed in the back of the block between the three test tubes and the color standards, and a piece of etched glass is placed

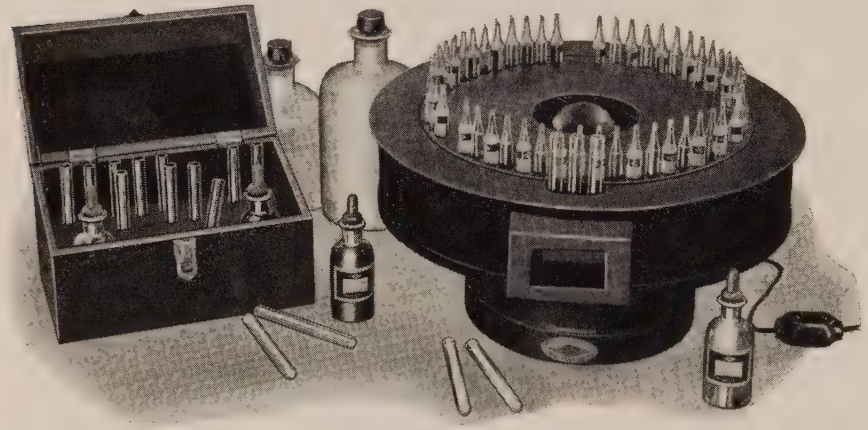

Fig. 319. LaMotte Roulette Comparator.

in a slot in the block directly in front of the three test tubes. The block also serves as a visor to cut out light from the outside. With this arrangement the observer always makes his readings under standard, diffused daylight conditions.

Any three sets of color standards such as chlorphenol red (pH 5.2–6.8), bromthymol blue (pH 6.0–7.6) and phenol red (pH 6.8–8.4) and 24 ampoules of distilled water, are supplied with the set. An extra polished wooden case, containing 50 ml. bottles of the corresponding indicator solutions, 1 empty 50 ml. bottle, 4–0.5 ml. pipettes with nipples, and 18 marked test tubes, is included as part of the equipment. A fabricoid cover is provided for the comparator.

The revolving drum contains three separate sets of holes, each set being designed to hold 9 color standards and 8 ampoules of distilled water. The color standards are placed in position in order alternating with the ampoules of distilled water. To make a determination three test tubes are filled with the solution to be tested and placed in the three holes in the block. Then 0.5 ml. of indicator solution is added to the middle tube and mixed thoroughly. The light is turned on and the drum revolved until the appropriate standards are behind the test sample. The standards are then shifted by turning the drum

until the color through the middle tube exactly matches that of one of the standards on either side of it or lies between them. The pH value is then read off directly from the color standards as the labels on the standards project above the top of the drum. In making a reading the drum must be turned so that an ampoule of distilled water is always directly behind the central test tube.

There is only room for three sets of color standards. Consequently, if the pH of the samples falls outside of the range of these three indicators, another set must be substituted for one of the sets present.

The individual color standards are contained in ampoules approximately 125 mm. long having an outside diameter of 15 mm. The test tubes are made to match the standards and are graduated at 10 ml. The color standards are guaranteed for one year.

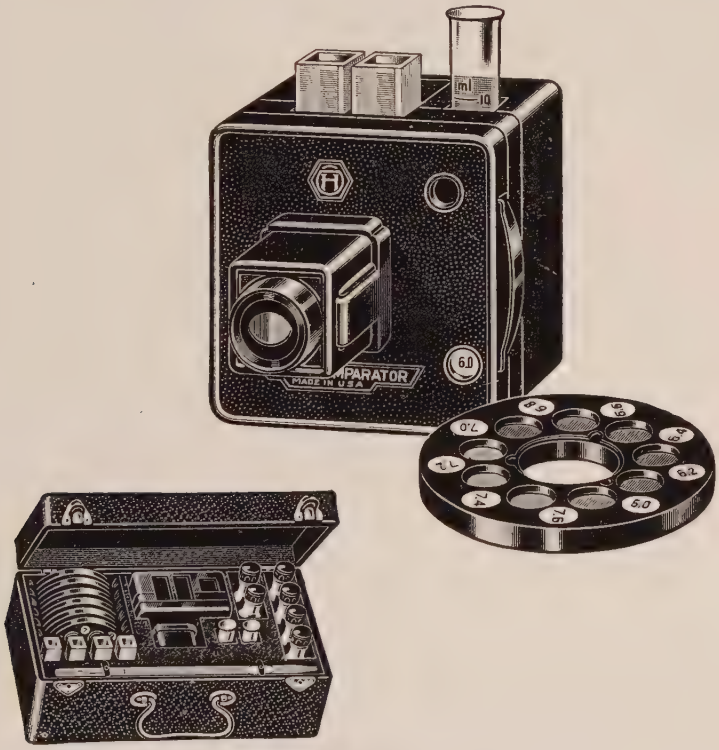

Fig. 320.

The Hellige Comparator

The Hellige Comparator (standard model) consists of a Bakelite housing with hinged front and rear covers and a dustproof enclosed prism for bringing the color fields into juxtaposition. Two acid-proof cemented cells with plane and parallel walls are provided. One cell is to receive the unknown solution

with indicator, the other to receive the test solution without indicator. This arrangement provides for color comparison with colored or turbid liquids as well as clear solutions.

In addition to the prism and cells the comparator is supplied with four round measuring tubes with graduations from 5 to 10 ml. in 1/1 ml. for measuring the test solution, 1 pipette with graduations 0.20, 0.25, 0.5 and 1.0 ml. for measuring the indicator solution, 1 opal glass plate, 50 ml. of indicator solution and 1 color disc.

Each color disc consists of a molded resin circular frame with a number (usually 9) of colored glass standards each one representing 0.2 pH so arranged that they can be revolved in the comparator. The color glass standards are made from variable layers of colored glass held together to simulate the colors resulting when buffer solutions of known pH are treated with the respective indicator. The value of each standard is placed on the disc so that it is visible in a special opening when that particular standard is in the reading position. Only one color standard is visible at a time. Separate color discs are provided for the various indicators.

An illuminator with stand can also be secured to provide the proper artificial illumination.

ELECTROMETRIC HYDROGEN ION MEASUREMENTS[1]

Electrometric hydrogen ion (pH) measurements are made with a suitable electrode system as the detecting unit and a potentiometer as the measuring unit. The electrodes develop a potential (e.m.f.) proportional to the pH of the solution being measured. The potentiometer measures e.m.f.

Potentiometric Principle

In order to determine the pH from the difference in potential of two electrodes, the voltage must be measured without allowing any appreciable current of electricity to flow from the cell, for with current flowing the voltage changes, owing to polarization effects at the electrodes. For this reason the measurement cannot be made with a voltmeter, because current is required to actuate such an instrument. The potentiometer is an ideal instrument for measuring voltage with no current flowing from the source. To show how this instrument operates, a brief explanation of the potentiometer principle is given here.

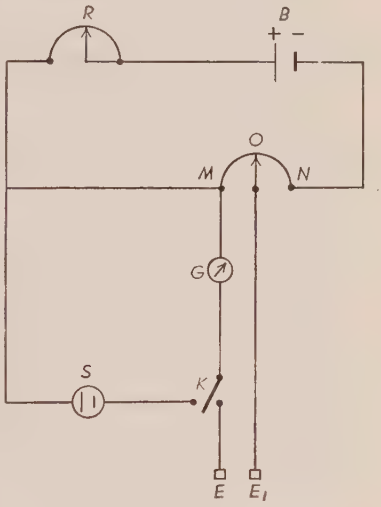

Fig. 321.

The slidewire MN, Fig. 321, represents an electrical conductor of uniform resistance, along which is placed a scale graduated in uniform divisions. The battery B causes a steady flow of electricity in this conductor. This is called the working current. The magnitude of this current can be changed by adjusting the rheostat R. With current flowing from M to N, M is positive with respect to any point O between M and N. Since the resistance is uniform, the fall of potential is uniform per unit length.

If EE_1 represents the cell for pH measurements the calomel electrode is the positive pole, which is connected to M through the galvanometer G. This puts like polarities in opposition. By adjusting the position of O the potential difference between M and O can be made exactly equal to that between E and E_1. When the voltages are balanced the deflection of the galvanometer is zero, and since this is a current indicating instrument, it proves that no current is flowing between the electrodes. Then if the fall of potential between M and O is known, the voltage of EE is measured without any flow of current from the electrodes.

[1] W. N. Greer, Leeds and Northrup Co.

The fall of potential between M and O is determined when there is a known potential difference between M and N. This is established by replacing the pH measuring electrodes with a standard cell S, by means of the switch K. If the voltage of the standard cell is, for example, 1.018 volts, the scale on MN is graduated in 1018 uniform divisions, and the current is adjusted by means of the rheostat R until the galvanometer shows no deflection. The potential difference between M and N is then 1.018 volts, and the fall of potential for each scale division is .001 volt, or 1 millivolt. If the pH cell is now substituted for the standard cell, the potential difference between the electrodes will be shown directly in millivolts by the number of scale divisions between M and O when they are adjusted for voltage balance.

The accuracy of the measurement depends upon the standard cell voltage and the uniformity of the slidewire (MN) resistance. Since this uniformity can be determined with practically any desired precision, the accuracy of measurement depends principally on the constancy of the standard cell voltage, and the method is therefore a primary method.

Potentiometers are available with various voltage ranges and accuracies, some designed for portable use. Tables or equations for converting voltage readings to pH values for all electrodes at various temperatures are obtainable. Some forms of potentiometers are calibrated directly in pH, means being provided to correct for solution temperatures.

In addition to the well-known standard types of potentiometers, there are coming into greater use vacuum tube potentiometers. These have been designed primarily for use with the high resistance glass electrode circuits. The resistances involved are too high to permit of the use of any except high sensitivity galvanometers, and only then with the low resistance glass electrode (2–6 Megohms). Due to the high resistances involved it is necessary that precautions be taken for properly shielding the potentiometer circuit. This is provided for in most of the commercially available instruments.

It is well to distinguish between accuracy and sensitivity. It is possible to have high sensitivity and low accuracy, and on the other hand to have conditions which would give high accuracy, if there were sufficient sensitivity. The sensitivity depends principally on the galvanometer used. If, with an arrangement not capable of very accurate results, a very sensitive galvanometer were used, its indications would be misleading if the sensitivity were not distinguished clearly from accuracy.

The most important factors affecting accuracy of results are the accuracy of the measuring instrument used, the character of the solutions being measured and the electrodes used, and the accuracy with which the reference electrode potential is known.

Electrode Systems

A single electrode is not sufficient for pH measurements because there is no convenient method for measuring its potential, but the potential of two electrodes, the absolute potential of one of which is known and is unaffected by pH, can be compared. It is therefore customary to use a fixed electrode as a reference, and to use as a measuring electrode one best suited to the measurement at hand.

For those who are not familiar with the theory relating e.m.f. of electrodes and pH, the reader is referred to the treatise on hydrogen-ion measurements by Clark, "The Determination of Hydrogen Ions," Williams & Wilkins.

Reference Electrodes: *Calomel Electrode.*—The calomel electrode is almost universally used as a reference electrode, due to its constancy of potential and ease of preparation. The calomel electrode is one in which mercury and calomel are in contact with a definite concentration of potassium chloride. These are contained in a vessel which may vary in design according to conditions of use. A common type of calomel electrode is shown in Fig. 322; a more recent design is shown in Fig. 323. The latter has the distinct advantage that the electrode, immersed in the test solution, is at solution temperature.

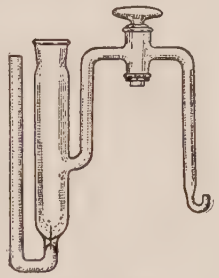

Fig. 322.

The potential of the mercury with respect to that of the solution depends on the concentration of mercurous ions from the calomel, but this is governed by that of chlorine ions, which are produced in the solution by potassium chloride as well as by calomel. The proportion of the total number of chlorine ions that is due to the potassium chloride varies with the KCl concentration. The voltage of the calomel electrode therefore depends on the concentration of potassium chloride in the electrode solution. Saturated, normal and tenth normal solutions are used.

Fig. 323.

The saturated calomel electrode is used more generally than either of the others. It is more easily prepared, and has some particular advantages.

Special precaution must be taken to prevent diffusion between the saturated solution of a salt bridge with the less concentrated solutions of the normal and tenth normal electrodes, whereas with the saturated electrode there is no tendency toward diffusion. When diffusion is prevented the potentials of the normal and tenth normal electrodes are fairly stable at room temperatures, but at higher temperatures it is difficult to prevent diffusion, with its resulting error in potential. The saturated electrode shows no change in potential between 5° and 60° C., other than that due to temperature. The temperature coefficient is approximately .8 millivolt per degree C. Another advantage of the saturated calomel electrode is that its conductivity is high, which makes for increased sensitivity.

An objection to the saturated electrode is that the solution may creep over the edge of the containing vessel with the resulting formation of masses of crystals. This is avoided in the design shown in Fig. 323, if the electrode is immersed in a container of distilled water when not in use.

For accurate and reliable potentials, extremely pure chemicals must be used in calomel electrodes. Mercury specially purified and calomel produced by electrolysis for the purpose can be commercially obtained in appropriate quantities, and their use is recommended. Chemically pure potassium chloride dissolved in distilled water is a suitable solution for use with them.

The saturated electrode is easily prepared. For a saturated KCl solution put the salt into warm distilled water in a beaker and stir it thoroughly with

repeated addition until no more of it will dissolve. Then stir in enough calomel to saturate the solution. A small quantity is sufficient as it is not very soluble. When the solution is cooled to room temperature, it should contain undissolved potassium chloride and calomel. Prepare enough solution to fill a reservoir for flushing the electrode from time to time. Add sufficient mercury (amount depends upon construction of electrode) to make contact with the platinum terminal, and sufficient calomel (HgCl) to assure saturation, an excess is advisable. Moisten with saturated KCl solution, shake vigorously, and then nearly fill with saturated KCl solution. If the electrode is not of the self-flushing type, care must be exercised in flushing the salt bridge occasionally.

Silver Chloride Electrode.—Comparable in principle to the calomel electrode is the silver-silver chloride electrode. It has largely been used in studies on activities of chlorides in solution, but recently has received increased attention as a reference in pH measurements. This electrode is not as readily prepared as is the calomel electrode, but it is highly reproducible, stable over extended periods of time, and has a small temperature coefficient.

The potential of the silver-silver chloride electrode depends upon the method of preparing the silver and the chloride. Methods have been described by Brown,[1] Harned,[2] McInnes,[3] Noyes and others.[4]

FIG. 324.

Measuring Electrodes.—There are a number of electrodes which have been used as pH measuring electrodes. Those which have been best established and most largely used will be described.

Hydrogen Electrode.—The hydrogen electrode consists of a noble metal coated with platinum black, immersed in the solution and under a definite partial pressure of hydrogen gas. Such an electrode is illustrated in Fig. 324. Means are provided for introducing the hydrogen gas, and allowing the gas to escape without forcing the solution entirely away from the metal.

Electrodes with large surfaces are generally not advisable as they are more difficult to saturate with hydrogen and therefore come to equilibrium less quickly.

In work with ordinary chemical solutions, and when high accuracy is not essential, the solution being measured may be contained in an open vessel, but the electrode potential will be slightly influenced by oxygen absorbed from the air. For precise work the vessel should be stoppered with provisions for carrying the electrodes through the stopper, and for allowing the gas to escape.

An electrode is said to be in equilibrium when its potential remains constant if the solution does not vary. The potential of the hydrogen electrode is not constant until the platinized surface is saturated with hydrogen, and any reducing action due to hydrogen is completed.

Limitations.—In some solutions, notably biological fluids, the platinum black may become clogged with substances which prevent absorption of hydrogen. The hydrogen electrode cannot be used in solutions containing strong oxidants like ferric ion, dichromates, nitric acid, peroxides and chlorine, nor in

[1] J. Am. Chem. Soc., **56**, 646 (1934).
[2] J. Am. Chem. Soc., **55**, 4849 (1933).
[3] J. Am. Chem. Soc., **37**, 1445 (1915).
[4] J. Am. Chem. Soc., **39**, 2532 (1917).

those containing strong reductants, such as sulfurous acid (SO_2) and hydrogen sulfide. Some organic compounds are very susceptible to reduction, particularly those of the aromatic series, such as azo benzene, aniline dyes and some unsaturated acids. In a solution containing either oxidizing or reducing compounds, a noticeable drift in the voltage occurs and a balance is difficult to obtain. The oxidizing or reducing action must be completed before the voltage is steady. The measurement is not trustworthy, for the pH value of the solution may be seriously changed in such reactions.

The hydrogen electrode cannot be successfully applied to solutions containing metal ions that fall below hydrogen in the electromotive series of metals and, also lead, all of which are reduced on the platinum electrode.

Platinizing the Electrodes.—The film of platinum black is deposited by electrolysis in 3% platinic chloride solution containing 1/40% lead acetate. The electrode should be thoroughly cleaned before platinizing. Using two dry cells in series it usually requires from 30 seconds to one minute to deposit the platinum black. Experience will determine the amount of plating necessary. The electrodes should be washed with distilled water, and immersed in distilled water when not in use. The electrodes should not be allowed to dry thoroughly.

Hydrogen Gas.—A very convenient source of hydrogen is the compressed gas supplied commercially in metal cylinders. A cylinder containing 100 or 200 cubic feet is commonly used in the laboratory, while small cylinders are available for portable use.

Compressed hydrogen produced by electrolysis may be sufficiently pure to use directly from the cylinder for measurements of ordinary accuracy, but it is common practice to pass it through solutions of potassium hydroxide and pyrogallol and then through water to remove traces of oxygen and other impurities that would affect the potential of the hydrogen electrode.

Quinhydrone Electrode.—Some of the difficulties encountered in the use of the hydrogen electrode are avoided by using a quinhydrone electrode. The basis of this electrode is a piece of platinum or gold the same as used for the hydrogen electrode, but the surface of the metal is not platinized and it is not supplied with gaseous hydrogen. Instead, a small quantity of quinhydrone (benzoquinhydrone) is dissolved in the solution, and in certain conditions the electrode in the solution acquires a potential that is definitely related to the hydrogen ion concentration of the solution. The potential is measured against that of a calomel electrode, and the pH value is found from the measured voltage in the same manner as with a hydrogen electrode.

Biilmann [5] was the first to describe the quinhydrone electrode for the pH measurements. Morgan, Lammert and Campbell [6] have published a series of papers covering detailed studies of this electrode. The quinhydrone electrode is quickly prepared, develops its potential rapidly and is not readily poisoned.

Rather than describe the method of preparing quinhydrone, it is suggested that this material be obtained from chemical manufacturers or suppliers of high grade chemicals.

Although the quinhydrone electrode can be applied successfully to many solutions containing oxidizing and reducing substances in which the hydrogen

[5] Ann. Chim. Phys., **15**, 109 (1921).
[6] J. Am. Chem. Soc., **53**, 2154 (1931) and **54**, 910 (1932).

electrode would give erroneous results, still it is not applicable in all cases. Measurements have been made with it on dilute nitric acid solutions, unsaturated organic acids, and on a variety of oxidizing systems that are of too low an oxidizing intensity to disturb the electrode potential.

Limitations of the Quinhydrone Electrode.—The quinhydrone electrode is not applicable over the entire pH range. In the acid range, 0 to 7 pH, it is excellent. In alkaline solutions strongly buffered, results of fair accuracy can be obtained to about 9 pH. In solutions poorly buffered, the upper limit is approximately 8.0 pH. In the latter case it is essential not to add an excess of quinhydrone, because it reacts with the alkali and changes the pH value of the solution. About 6 to 8 drops of a saturated solution of quinhydrone in acetone is sufficient for 50 ml. of test solution.

If the pH value of a solution measured with a hydrogen electrode differs from that with a quinhydrone electrode, the difference may be due to the "salt error" in the quinhydrone value. The hydrogen electrode is assumed to have no salt error. The magnitude and sign of the salt error (positive or negative divergence from the correct pH value) of the quinhydrone electrode depends upon the type and concentrations of the salts present in the solution. The salt error in nickel plating solutions of total salt concentration about 2.0 N is below +0.05 pH. In a 10.0 N ammonium sulfate solution it is approximately −0.2 pH, while in a 4.0 N sodium chloride solution it is approximately +0.2 pH. Since most solutions are far more dilute than these, the salt error is generally negligible.

In high purity (99%) sugar solutions the quinhydrone electrode gives values which are approximately .2 pH low, while on low purity products, such as molasses, the values are high. Over purity ranges of 80% to 97% the quinhydrone electrode gives good results.

Antimony Electrode.—Of the various metal and metal oxide electrodes that have been described, the antimony electrode has proved to be the most satisfactory. It does not require gas or a catalytic surface as does the hydrogen electrode; it does not require the addition of a reagent as does the quinhydrone electrode. The antimony electrode is not readily prepared, but once made up is useable for very extended periods. It may be obtained commercially ready for use. It is a rugged electrode and in certain designs is used industrially for continuous plant service. The inherent accuracy of the antimony electrode is not as great as is the hydrogen or the quinhydrone electrode.

Its limitations have been described by Perley.[7] Notable among these is that the e.m.f.-pH relation varies with the degree of buffering of the solution, and that the degree of saturation with air, particularly below 7 pH, affects the potential-pH relationship. The antimony electrode is not applicable to solutions which are oxidizing or are strongly reducing, nor in solutions containing more than a trace of copper, silver, or other metals below antimony in the electrochemical series of the elements. However, under known conditions this electrode serves a very useful purpose in measuring pH over the range of 3 to 12 pH. It is being used quite extensively in sugar solutions (beet, raw cane, and refinery), paper mills, water treatment, pigments, etc. For measurements on a given sample extending over long periods of time, this electrode is particularly suitable.

[7] Trans. Am. Inst. Chem. Engrs., **29** (1933).

Glass Electrode.—The work of Hughes,[8] Kerridge,[9] McInnes and Dole,[10, 11] and others have shown the possibilities of the glass electrode as a pH measuring electrode. The glass electrode consists, primarily, of a thin membrane of glass, of a definite composition (72% SiO_2, 22% Na_2O, 6% CaO), one side of the membrane being exposed to the solution being measured and the other side exposed to a standard reference solution. The membrane is made up in the form of a bulb, with a reference electrode and solution on the inside. The bulb, along with a reference electrode, is immsered in the solution to be tested. The glass electrode, which behaves like a hydrogen electrode, is thus interposed between two fixed electrodes.

A high sensitivity galvanometer, or an electrometer potentiometer, is required to measure pH with the glass electrode due to its high resistance. Glass electrodes and suitable measuring devices are commercially obtainable.

The glass electrode is particularly suitable for pH measurements in the presence of oxidizing and reducing solutions, where other types of electrodes give erroneous results. It also is the best type of electrode to use in unbuffered solutions, since the introduction of the glass bulb into an unbuffered solution does not change the pH of the latter. The electrode is stable over rather long periods, the life of the electrodes being largely determined by crystallization of the glass. The characteristics of the internal reference element and solution determine how often they must be replaced.

The glass electrode, in some forms, is rather fragile and must be handled with care. In other forms, with heavier glass wall, the electrode often exhibits an asymmetry potential; that is, it differs from the Nernst equation by more or less constant potential. The E.M.F.-pH relationship of the glass electrode is linear up to pH 9.6, above which it may be used with a special calibration to 12.5 pH. The greatest deviation from linearity is obtained in solutions containing sodium ion concentrations in excess of 0.1 molal.

The electrode can be made in small sizes, permitting of measurements on minute samples. It has a further advantage in that it does not contaminate the solution being measured, should only limited samples be available, and it is necessary to make other determinations on the same material.

Working Formulae for pH Electrodes

1. Hydrogen-Saturated Calomel.

$$\mathrm{pH} = \frac{V - 0.2648 + .00076t}{0.0001983T},$$

at 25° C.,

$$\mathrm{pH} = \frac{V - .2458}{.0591}.$$

2. Quinhydrome-Saturated Calomel.

$$\mathrm{pH} = \frac{V + 0.4529 + .00002t}{0.00019832T},$$

[8] J. Am. Chem. Soc., **44**, 2860 (1922).
[9] Biochem. J., **19**, 611 (1935).
[10] Ind. Eng. Chem. Anal. Ed., **1**, 57 (1929).
[11] J. Am. Chem. Soc., **53**, 3315 (1931).

at 25° C., $$\text{pH} = \frac{V + .4534}{.0591}.$$

3. **Glass-Saturated Calomel.**—When using quinhydrone-1 pH hydrochloric acid as reference in glass electrode, use formula as applied to (2) Quinhydrone above, up to 9.6 pH. Relation is non-linear above 9.6 pH in the presence of sodium ions.

4. **Antimony-Saturated Calomel.**

Buffered solutions at 25° C.

Below pH 7, $$\text{pH} = \frac{V + .0157}{.0591},$$

Above pH 7, $$\text{pH} = \frac{V - .0292}{.0527}.$$

V = Observed potential in volts,
t = ° C.,
$T = 273.1 + t$.

POTENTIOMETRIC METHODS [1]

Measurements of the electromotive forces of electrolytic cells may be used in analysis for two closely related purposes: (*a*) the determination of the concentration (or activity) of some kind of ion. The concentration of hydrogen ion, or the pH of a solution, is frequently estimated by this means as has been described in the preceding chapter. (*b*) The determination of end-points in titrations.

The principle of the *potentiometer* has been explained in the preceding chapter.

Single Electrode Potentials.—The E.M.F. of a cell may be considered to be made up of the following effects:

Total E.M.F.

Electrode I | Solution I || Solution II | Electrode II.

a b c

The total effect is: E.M.F. $=(a-c)\pm b$. The sign of c may be different from that of a. For example, the values for copper and zinc are respectively $+0.344$ and -0.762 under certain conditions; in this case E.M.F. $=0.344-(-0.762)=1.106$ volts. The liquid junction effect b between the two solutions is due to different mobilities of the various ions; it is frequently small (1–3 millivolts), and is ignored in most analytical determinations. In precise work the effect may be measured, or taken into account by a calculated correction.

If one of the electrodes, for example, II, is a constant, or reference electrode, the changes in total E.M.F. of the cell measure essentially the variations which occur at electrode I.

Suppose that electrode I consists of a metal in contact with a solution of its ions, for example silver in contact with a solution of silver nitrate. In such an instance Nernst found that the effect at a single electrode could be represented by:

$$E_{\mathrm{I}}=E_0+\frac{RT}{nF}ln\ [\mathrm{Ion}],$$

where R is the gas constant, T the absolute temperature, n the number of Faradays concerned in the transfer of 1 gram ion to one gram atom, or vice versa, and F the Faraday $=96{,}540$ coulombs, ln the natural logarithm, and [Ion] the molecular concentration of the ion. Upon converting to common logarithms (base 10) and substituting for R its value 8316 volt-coulombs, we have:

$$E_{\mathrm{I}}=E_0+\frac{0.000198\ T}{n}\log\ [\mathrm{Ion}].$$

For silver, for example, $E_{\mathrm{Ag}}=0.798+0.0591\log\ [\mathrm{Ag}^+]$ (at 25° C.). The convention regarding the sign of the electromotive force here used is the opposite

[1] N. Howell Furman, Professor of Chemistry, Princeton University, Princeton, N. J.

of that given by Nernst; we use the sign of the metal relative to the solution, which is the convention adopted by foreign and American electrochemical societies.

This electrode potential expression is not limited to substances which can be formed into solid electrodes. For example, platinized platinum catalyzes the reversible exchange of hydrogen atoms to hydrogen ions, and a hydrogen electrode may be formed by causing hydrogen gas to stream through a solution into which a lightly platinized platinum, gold, or iridium electrode is dipped. At 1 atmosphere pressure of hydrogen gas:

$$E_H = 0.0000 + 0.0591 \log [H^+] \text{ (at 25° C.)}.$$

The E_0 value of the hydrogen electrode is arbitrarily chosen as the standard of reference, and is set equal to zero. The E_0 value of any other substance is then found from the measured value of E (with reference to the hydrogen standard) when the concentration of the ion in question is equal to 1 molar.

If we are dealing with a negative ion, the sign of the second term in the electrode expression is negative. For the chlorine electrode: $E_{Cl} = E_0 - 0.0591 \log [Cl^-]$ (at 25° C.).

The E_0 value is characteristic for each substance and is a measure of the relative oxidizing or reducing power of the substance relative to hydrogen.

It should be noted that Nernst derived the electrode potential formula on the basis of ideally dilute solutions, and that the electrode potential is really a function of the activity rather than the concentration of the ion in question. Hydrogen ion concentration measurements are standardized at present on E.M.F. measurements, or in other words on an empirical activity basis, since the point of reference of the whole system is based on hydrogen-ion concentration values calculated from conductance measurements. Kolthoff gives the relation between the exponents of the activity and ion concentration values as:

$$paH = pH + 0.04.^2$$

As far as the potentiometric determination of end-points of volumetric reactions is concerned, activity relations need not be taken into account.

Oxidation-Reduction Electrodes.—A burnished platinum electrode may, when dipped into a solution containing an oxidizing agent and its reduction product, assume a potential which is a measure of the reversible oxidation-reduction power of the solution. Peters [3] found that for the reversible ferric-ferrous ion system, the relations were expressed by the formula:

$$E = E_0 + 0.0591 \log \frac{[Fe^{+++}]}{[Fe^{++}]} \text{ (at 25° C.)}.$$

In this case the E_0 value is equal to the observed value when $[Fe^{+++}] = [Fe^{++}] = 1$ (the normal oxidation-reduction potential).

In general, for a reversible oxidation-reduction equilibrium:

$$Ox + nF \rightleftharpoons Red,$$

in which Ox represents oxidizing agent, Red its reduction product, F the Fara-

[2] I. M. Kolthoff, Rec. Trav. chim., **49**, 401 (1930).
[3] R. Peters, Z. physik. Chem., **26**, 193 (1898).

day, and n the number of Faradays per gram ion of oxidizing agent, we have, if the electrode process is reversible:

$$E = E_0 + \frac{0.0591}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \text{ (at 25° C.).}$$

The E_0 value is an important characteristic constant for each system, and is referred to that of the normal hydrogen electrode as zero.

If the partial oxidation-reduction reaction involves hydrogen or hydroxyl ion, we obtain an electrode expression that includes the concentrations of these ions. For example:

$$MnO_4^- + 8H^+ + 5\ominus \rightleftharpoons Mn^{++} + 4H_2O,$$

$$E = E_0 + \frac{0.0591}{5} \log \frac{[MnO_4^-]\,[H^+]^8}{[Mn^{++}]}.$$

The concentration of water is practically constant for dilute aqueous solutions, and hence its actual value need not be introduced in determining the E_0 value for the system.

Reference Electrodes.—The concentration of a metallic ion in contact with an electrode of the metal may be kept constant by covering the metal with a suspension of one of its slightly soluble salts in a solution containing an anion

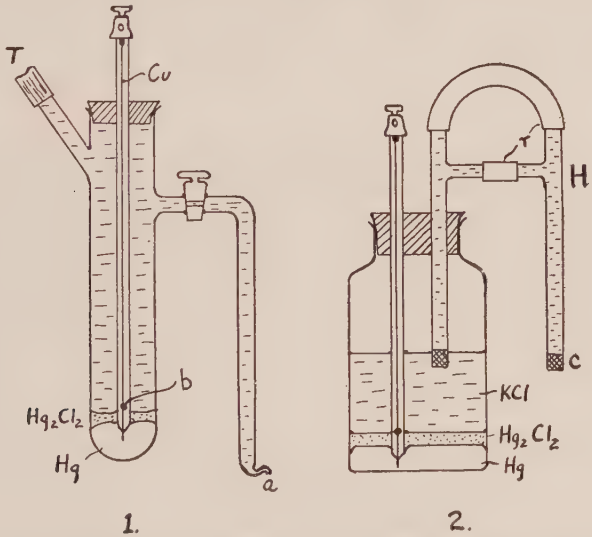

FIG. 325.—Calomel Electrode Vessels. (1) Modified Ostwald Type. The mercury is overlain with calomel intimately mixed with mercury; the potassium chloride solution is introduced through tube, T. The side tube at a ends in a capillary, or a porous plug to prevent diffusion. Contact with the mercury is made by a platinum wire sealed through a glass tube, and joined at b to a copper wire. (2) Represents the bottle type electrode recommended by E. Müller. The siphon tube, H, is made of two glass T-tubes, joined by rubber tubes, r. The bottom of each tube is plugged at c with agar jelly made up in potassium chloride solution of the strength needed for the electrode (0.1 N, N, etc.).

in common with the precipitate. The calomel electrode consists of a mercury electrode in contact with a potassium chloride solution that is saturated with calomel, Hg_2Cl_2. The concentration of mercurous ions is therefore constant at constant temperature, and hence a calomel half-cell serves as a constant, or reference electrode. Some convenient types of half-cells are shown in Fig. 325. The concentrations of potassium chloride that are most frequently used are: (i) 0.1 N, (ii) N, (iii) 3.5 N, or (iv) a saturated solution.

Values for Various Calomel Electrodes
(Referred to N hydrogen electrode as zero)

Concentration of KCl	E_{Calomel} in Volt
0.1 N	$0.3380-0.00006\ (t-18)$
1 N	$0.2864-0.00024\ (t-18)$
3.5 N	$0.2549-0.00039\ (t-18)$
Saturated	$0.2504-0.00065\ (t-18)$

Here t represents degrees Centigrade (applicable between 10° and 30°).

Other electrodes that are frequently employed are the silver electrode in contact with silver chloride and a potassium chloride solution of definite concentration. When the presence of chloride is undesirable a salt bridge of sulfate or nitrate may be interposed between the reference electrode and the solution. A mercury-mercurous sulfate-sulfuric acid electrode is convenient for reference purposes in the study of oxidation-reduction processes in the absence of chloride.

Potentiometric Titrations

If the E.M.F. of a cell composed of two electrodes dipped into an unknown solution is measured during a titration, the plot of E.M.F. readings as ordinates against ml. of standard solution as abscissas gives in general an abrupt change in potential at the analytical end-point of the reaction at the end-point. One electrode serves as an indicator of changes in ion concentration, and the other electrode is a calomel, or other reference electrode. The indicator electrode must be appropriate for the particular type of reaction involved. The solution must be well stirred during the titration, preferably by a motor-driven stirrer. If the standard solution is added in small equal increments near the end-point, say 0.05 ml. at a time, the end-point is in general marked by a maximum change of E.M.F. per small increment of reagent. That is, the plot of $\frac{\Delta \text{ E.M.F.}}{\Delta \text{ ml.}}$ against ml. of reagent gives a maximum at the end-point. In favorable cases it is not even necessary to record the readings near the end-point, although this is advisable until some experience has been had with a particular type of titration. The outstanding advantages of the potentiometric method are (1) applicability to colored solutions; (2) precision of determination of end-point; (3) the possibility of obtaining a succession of end-points, and hence the determination of two or more substances by a single titration.

A type of assembly which is suitable for general study of potentiometric titration processes is shown in Fig. 326. If it is not desired to determine the

exact voltage range for a given process, the potentiometer may be replaced by a simple slide wire potentiometer, and the use of the standard cell may be omitted. Some still simpler forms of apparatus are described on p. 2318. One of the types of titration cell which may be used when air must be excluded is shown in Fig. 327. The vessel shown in Fig. 328 may be used for hydrogen electrode titrations if an opening is provided in the stopper for a burette.

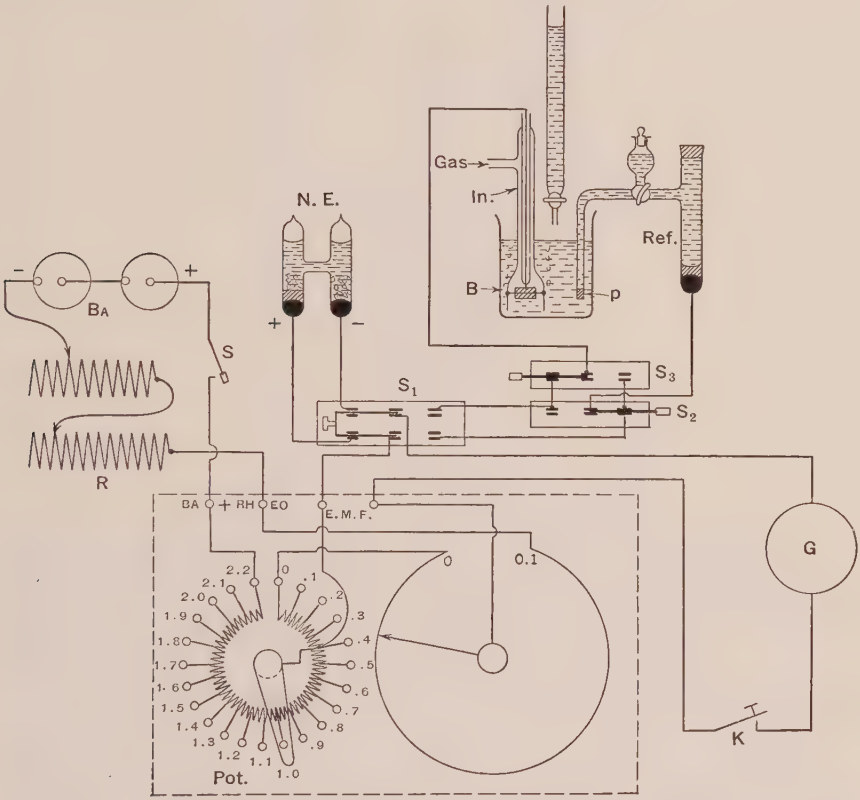

FIG. 326.—Potentiometric Titration Circuit. *Ba*, battery; *R*, resistance; *S*, battery switch; *Pot.*, potentiometer; *N.E.* standard cell; S_1, reversing switch; S_2, S_3, single-pole double-throw switches; *In.*, indicator electrode; *Ref.*, reference electrode; *B*, beaker containing solution to be titrated; *p*, porous plug, or capillary. In most cases a motor-driven stirrer is essential. (Furman, J. Chem. Educ., **3**, 932 (1926).)

Neutralizations.—A calomel electrode is in general suitable for reference. The indicator electrode may be any one of the following:

Hydrogen Electrode.[4]—The solution should be free from powerful oxidizing and reducing agents, for example, permanganate, bichromate, ferric iron, nitric

[4] General literature references: Böttger, Z. physik. Chem., **24**, 253 (1897); Hildebrand, J. Am. Chem. Soc., **35**, 869 (1913); H. S. Britton, J. Chem. Soc. (London), numerous articles, 1924–1927.

acid, ions of metals like Ag, Cu which are precipitated, easily reducible organic compounds, the alkaloids, certain dyestuffs.

Quinhydrone Electrode.[5]—May be used in the titration of acid solutions which are free from strong oxidizing and reducing agents. May be used for alcoholic solutions.

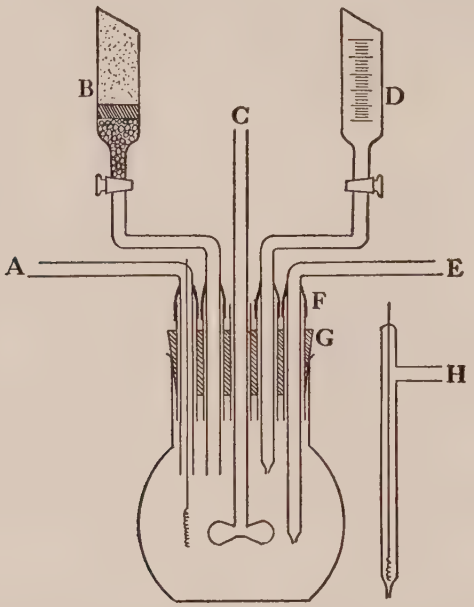

FIG. 327.—Titration Vessel. *A*, inlet for inert gas, also used as electrode holder; *B*, reductor, or other form of special apparatus used in introducing sample; *C*, motor-driven stirrer; *D*, burette; *E*, tube leading to reference electrode; *H* is a sheltered platinum electrode to be inserted in place of *E*, when the differential method is used. The stopper, *G*, is bored to give any desired number of openings, through which glass tubes are placed. The rubber tubes at *F* join the various pieces of apparatus to the glass tubes carried by the stopper. The gas escapes around the shaft of the stirrer, *C*. (Furman and Schoonover, J. Am. Chem. Soc., **53**, 2561 (1931)).

Antimony Electrode.[6]—A rod of cast antimony is used; some antimony trioxide, preferably of the stable cubic form, should be present. The electrode may be used for titrations where the hydrogen electrode applies, and also for determining end-points when strong oxidizing agents are present.

Oxygen, or Air Electrode.[7]—May be used for all ordinary titrations and also in the presence of oxidizing agents.

[5] Kolthoff, Rec. Trav. Chim., **42**, 186 (1923); LaMer and Parson, Proc. Expl. Biol. Med., **20**, 239 (1923); J. Biol. Chem., **57**, 613 (1923); Auerbach and Smolczyk, Z. physik. Chem., **110**, 65 (1924); Baggesgaard-Rasmussen and Schou, Z. Elektrochem., **21**, 189 (1925); Wagener and McGill, J. Am. Pharm. Assoc., **14**, 288 (1925); Klit, Z. physik. Chem., **131**, 61 (1927).

[6] Uhl and Kestranek, Monatsh., **44**, 29 (1923); Kolthoff and Hartong, Rec. Trav. Chim., **44**, 113 (1925); Britton and Robinson, J. Chem. Soc., p. 458 (1931).

[7] Furman, J. Am. Chem. Soc., **44**, 2685 (1922); Trans. Am. Electrochem. Soc., **43**, 79 (1923); Britton, J. Chem. Soc., **125**, 1572 (1924); **127**, 1896, 2110 (1925).

Glass Electrode.[8]—Suitable in the presence of oxidizing or reducing agents. A special electrical measuring system including either a quadrant electrometer or a vacuum tube voltmeter is usually required because of the high resistance of the electrode. However with low-resistance glass films (2–5 megohms) a simple potentiometer and a high resistance galvanometer may be used.

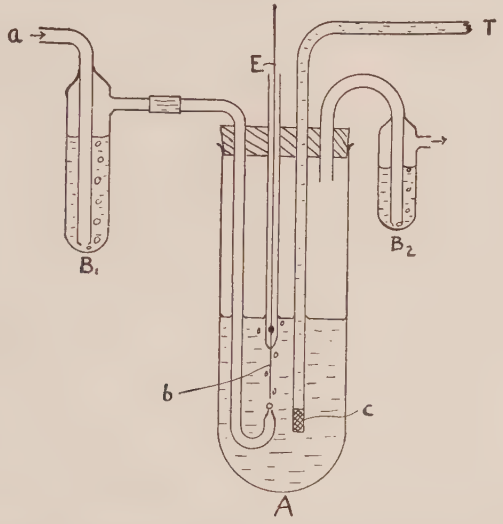

FIG. 328.—Cell for pH Measurement. Pure hydrogen enters a bubbler, B_1, at *a*. B_1 is filled with some of the solution whose pH is measured; the latter is put in vessel *A*, and is saturated with hydrogen. The gas comes in contact with the lightly platinized wire or foil *b*, which is of platinum, and is sealed into a glass tube, where contact is made with the copper wire, *E*. The hydrogen escapes through the bubbler, B_2. The tube, *T*, is filled with potassium chloride solution, and leads to the calomel electrode; *c* is a porous plug, or capillary to prevent diffusion.

Additional metal-metal oxide electrodes which serve as hydrogen-ion indicators are known (mercury-mercuric oxide, copper-copper oxide, bismuth-bismuth oxide, tellurium-tellurium oxide, etc.) but do not appear to offer any decided advantages over those mentioned.[9]

Some graphs of hydrogen electrode titration data are shown in Fig. 329 together with graphs of indicator transition intervals. Titration curves of similar form are obtained when other indicator electrodes are used.

The electrometric method is superior to indicator methods when the solution is highly colored; it also appears to offer decided advantages in estimating small amounts of weak acids (see "differential method," p. 2318).

[8] Haber and Klemensiewicz, Z. physik. Chem., **67**, 385 (1909); Hughes, J. Am. Chem. Soc., **44**, 2860 (1922); J. Chem. Soc., p. 481 (1928); see Kolthoff and Furman, "Potentiometric Titrations," 2nd. Ed., 1931, for further bibliography and description of apparatus.

[9] See Kolthoff and Furman, "Potentiometric Titrations," for a review of the literature.

Potentiometric neutralizations may be made in many anhydrous solvents, as, for example, ethyl alcohol,[10] amyl alcohol,[11] glacial acetic acid,[12] etc.

Precipitations and Complex Formations

The reference electrode may be a calomel half cell, with a suitable salt bridge interposed if the presence of chloride is harmful. Theoretically any sufficiently

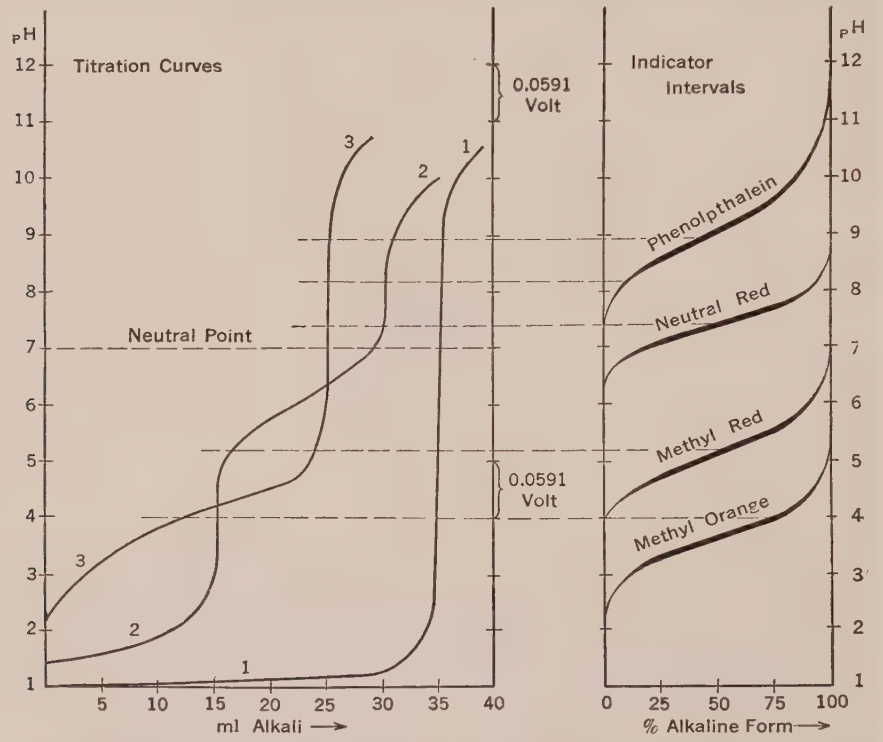

Fig. 329.—Titration Curves and Changes of Indicators.—Curve 1, approx. 0.1 N sulfuric acid titrated with equivalent alkali; (2) 40 cc. 0.0711 N phosphoric acid titrated with 0.2 N NaOH (Davis, Oakes, Salisbury, Ind. Eng. Chem., **15**, 182 (1923)). (3) 25 cc. 0.5 N acetic acid with 0.5 N NaOH. The dotted lines leading from the right of the figure represent approximately the mid-points of the visible indicator changes.

unattacked metal or non-metal might serve as an indicator electrode. Practically, only a few have been used successfully, notably the silver, mercury or iodine electrodes. These electrodes serve for the titration of halides with silver nitrate, or with mercury salts, or for the determination of silver or mercury with

[10] Bishop, Kittredge and Hildebrand, J. Am. Chem. Soc., **44**, 135 (1922).
[11] Seltz and McKinney, Ind. Eng. Chem., **20**, 542 (1928).
[12] Hall and Conant, J. Am. Chem. Soc., **49**, 3047 (1927); Conant and Hall, ibid., **49**, 3062 (1927); Hall and Werner, ibid., **50**, 2367 (1928); see Clark, "Determination of Hydrogen Ions," and Kolthoff and Furman, "Potentiometric Titrations," 2nd Ed., for further references.

halides. Fig. 330 shows the graph of the data obtained in the titration of a mixture of iodide and chloride with silver nitrate. This type of process is the more accurate: (*a*) the more concentrated the solution, provided adsorption phenomena can be dealt with satisfactorily; (*b*) the less soluble the precipitate.

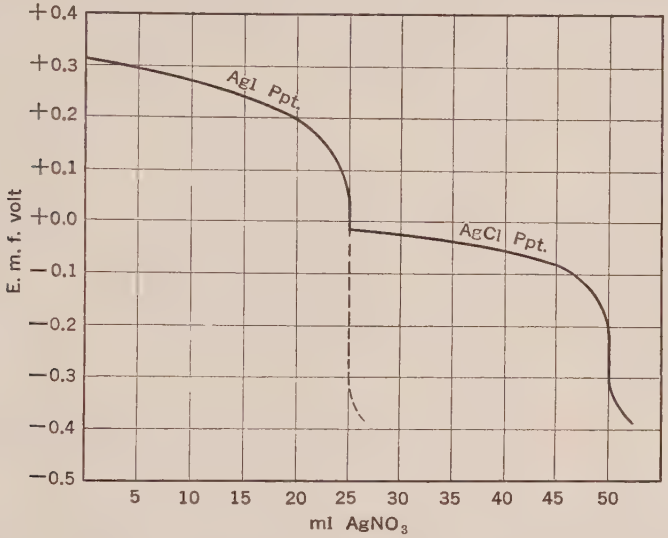

FIG. 330.—Titration of Mixture of Chloride and Iodide with Silver Nitrate. 25 cc. of approx. 0.1 N KI plus 25 cc. approx. 0.1 N KCl titrated with silver nitrate. The dotted curve shows the graph obtained when iodide alone is present.

The silver electrode indicates the end-point of the important complex formation process: $Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$. When this process is complete further addition of silver ion gives a flat curve during the precipitation of silver cyanide, followed by an abrupt change at the end of this second process. This reaction may be used in the indirect determination of nickel, or in the estimation of silver halide in a photographic emulsion.[13]

The titration of halide with silver may be carried out potentiometrically with atomic weight precision. The potentiometric method offers especial advantages in examining mixed halides (Clark, loc. cit.).[14]

The end-points of ferrocyanide precipitations may be determined with an oxidation potential indicator electrode (cf. next section). The ferrocyanide solution is prepared with a small amount of ferricyanide present. As long as ferrocyanide ions are removed by the formation of the precipitate, the potential

[13] See W. Clark, J. Chem. Soc. (London), p. 768 (1926).

[14] References on halide titrations: Behrend, Z. physik. Chem., **11**, 466 (1893); Liebich, Dissertation, Dresden, 1920; Treadwell, Janett and Blumenthal, Helv. Chim. Acta, **6**, 513 (1923); E. Müller, Z. Elektrochem., **30**, 420 (1924); Phot. Ind., **18**, 14 (1924); Clark, J. Chem. Soc. (London), p. 768 (1926); Lange and Schwartz, Z. Elektrochem., **32**, 240 (1926); Z. physik. Chem., **129**, 111 (1929); MacInnes and Dole, J. Am. Chem. Soc., **51**, 1119 (1929); Tomicek, Collect. Czechoslovak Chem. Commun., **1**, 443, 585 (1929); **2**, 1 (1930); Tomicek and Jansky, ibid., **1**, 582 (1929).

remains in the oxidizing region; as soon as the first excess of ferrocyanide is present there is a sharp drop in the E.M.F. of the titration cell.

The titration of zinc with ferrocyanide has been studied by a number of investigators, and many conflicting statements and conclusions occur.[15] The solution should be only slightly acid; the titration is more rapid at 65° than at room temperature, but there is danger of overstepping the end-point even at the higher temperature. Kolthoff and Verzijl found that in the titration of 100 ml. of 0.1 N zinc sulfate the error was as follows:

Temperature °C.	Substance Added	Error in Per Cent of ml. of Reagent Required
15.....	(Neutral sol'n)	−1.04
65.....	(Neutral sol'n)	−0.9
15.....	0.12 N sulfuric acid	−0.77
65.....	0.12 N H_2SO_4, 3 g. K_2SO_4	−0.4
65.....	5 g. K_2SO_4	−0.45
15.....	10 g. ammonium chloride	−2.25
65.....	10 g. ammonium chloride	−0.8
15.....	20 g. ammonium sulfate	−0.05
65.....	20 g. ammonium sulfate	−1.15

From Potentiometric Titrations, 2nd Ed., Kolthoff and Furman.

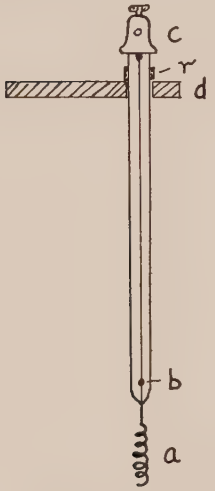

Fig. 331. — Oxidation-Reduction Indicator Electrode. *a* represents about 5″ of No. 28 B. and S. platinum wire sealed through a glass tube and fused at *b* to a copper wire, which leads to the binding post *c*. The rubber tube, *r*, supports the electrode on the bakelite plate, *d*, which may be drilled to carry a number of electrodes of the construction shown.

Large amounts of calcium and magnesium cause errors; addition of fluoride prevents the interference of ferric ion. Manganese must be removed before the titration.

With potassium ferrocyanide the precipitate is $K_2Zn_3(Fe(CN)_6)_2$, whereas with other alkali metal ferrocyanides the precipitate has a different composition. From all of the considerations which have been presented it is evident that good results will be obtained only under carefully standardized experimental conditions.

Cadmium and lead may be determined by ferrocyanide precipitation, but silver and copper give erratic results.[16]

Oxidation - Reduction Reactions. — The indicator electrode is of burnished platinum, either wire, foil or gauze. Fig. 331 represents the construction of one satisfactory type of electrode. A calomel or a mercury-mercurous sulfate and sulfuric acid reference electrode may be used.

The reagent may be any sufficiently stable oxidizing or reducing agent, and each reagent may be used to determine one or more substances in a single

[15] Knauth, Dissertation, Dresden, 1915; von Bischowsky, Ind. Eng. Chem., **9**, 668 (1917); Hedrich, Dissertation, Dresden, 1919; Kolthoff, Rec. Trav. Chim., **41**, 425 (1923); Kolthoff and Verzijl, ibid., **43**, 380 (1924); Fr. Müller, Z. anorg. allgem. Chem., **128**, 126 (1923); E. Müller and Gäbler, Z. analyt. Chem., **62**, 29 (1923); Treadwell and Chervet, Helv. Chim. Acta, **5**, 633 (1922); **6**, 550, 559 (1923).

[16] See Kolthoff and Furman, "Potentiometric Titrations," pp. 331–333, 2nd Ed., 1931, for determination of cerium, lanthanum, gallium, and indium by ferrocyanide precipitation.

titration. In Fig. 332 is shown the determination of iron, vanadium, and uranium by a single titration of the reduced solution with permanganate. The uses of potassium permanganate, bichromate, iodate, bromate or ceric sulfate have been intensively studied, and the potentiometric method offers the advantages of accuracy, speed, and usefulness in highly colored solutions. The powerful reducing reagents, chromous, titanous, or stannous chloride, arsenious acid, and ferrous sulfate have decided advantages in certain fields of industrial analysis. We shall describe only those methods which are useful in steel analysis.

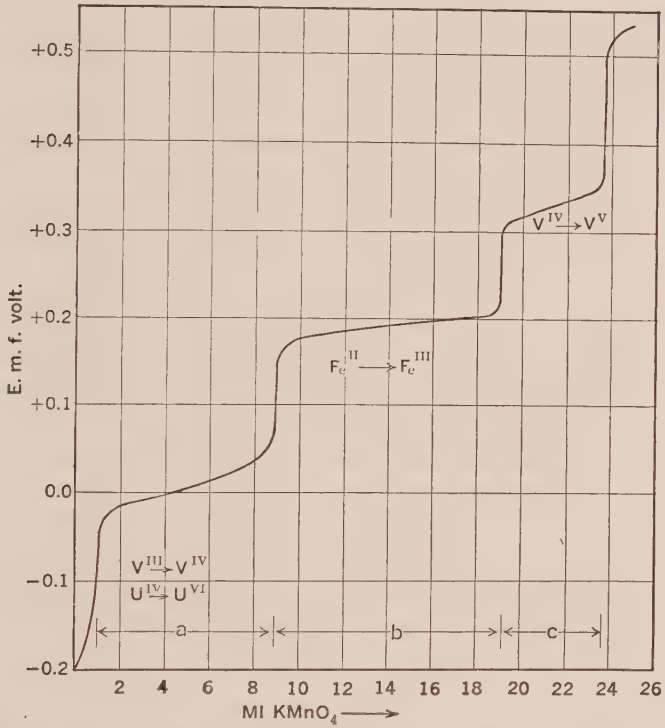

Fig. 332.—Simultaneous Determination of Reducing Agents. From data of Müller and Flath, Z. Elektrochem., 29, 503 (1923). The cc. of permanganate given by (*a–c*) correspond to oxidation of U^{IV} to U^{VI}; *b* cc. are equivalent to the iron, and *c* cc. to the vanadium.

Determination of Chromium and Vanadium in Alloys.—The pioneer work in this field was done by Kelley and his associates.[17] It was found possible to balance the E.M.F. of the cell approximately during the titration. The end-point was then marked by a single permanent galvanometer deflection. Kelley

[17] Kelley and Conant, J. Am. Chem. Soc., **38**, 341 (1916); Ind. Eng. Chem., **9**, 780 (1917); Kelley, Wiley, Bohn and Wright, Ind. Eng. Chem., **13**, 939 (1921); **11**, 633 (1919); Kelley and Wiley, Ind. Eng. Chem., **13**, 1053 (1921).

devised an electrotitration apparatus in which this principle of operation may be most easily used. More recent work has led to improved and more selective oxidation methods prior to titration.[18] The following procedures are those of Willard and Young. They found that potassium bromate oxidizes vanadium selectively in the presence of chromium if the solution contains a definite concentration of hydrochloric acid.

$$2KBrO_3 + 10VOSO_4 + 14H_2O = 10HVO_3 + Br_2 + K_2SO_4 + 9H_2SO_4.$$

Vanadium in Chrome-Vanadium Steels.—A sample of 4 or 5 g. is convenient when the percentage of vanadium is low (0.15 to 0.25%). Place it in a 600-ml. beaker, add 30 to 35 ml. of water and run in 1.5 ml. of sulfuric acid, sp.gr. 1.83, for each gram of steel, and 3 to 4 ml. of acid in addition, to speed the solution. After the steel has completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 ml. of water and heat until the salts have dissolved. Add nitric acid, sp.gr. 1.42, drop by drop to the hot liquid until the violent oxidation of ferrous sulfate is over (3 to 3.5 ml. of acid are sufficient). Boil the solution to destroy oxides of nitrogen, dilute to 200 ml., and add to this solution which should be at room temperature, 6 ml. of hydrochloric acid, sp.gr. 1 18 (if a 4 or 5 gram sample is used; with a smaller sample more acid must be added: 9, 12 and 14 ml respectively for 3, 2 and 1 g. of iron), 5 g. of ammonium sulfate, and 1.5 to 2 g. of potassium bromate. Leave the material on the low temperature hot plate for 15 minutes, by which time it should reach approximately 65° C., boil 10 minutes to destroy excess bromate, cool in ice to 5° C., add 25 ml. of ice-cold sulfuric acid, sp.gr. 1.5, and titrate with 0.025 N ferrous sulfate.

Vanadium in Chrome-Vanadium-Tungsten Steels.—The sample may vary conveniently from 1.5 g. for a steel containing 1% or more of vanadium to 3 g. for 0.2% of vanadium. Add 25 to 30 ml. of water to the weighed sample in a 400-ml. beaker. Use 1.5 ml. of sulfuric acid, sp.gr. 1.83, for each gram of steel and 3 to 6 ml. excess. Warm gently until there is no further evolution of hydrogen. Boil over a free flame until salts begin to separate in order to assist in breaking up carbides, dilute to about 50 ml. and boil until salts have dissolved. Add to the boiling hot solution nitric acid of sp.gr. 1.42, drop by drop, until the violent action is over, then 5 to 6 ml. in excess. Boil down until tungstic acid separates out in considerable amount and becomes yellow; dilute somewhat with hot water, let settle, and filter the tungstic acid, using hot 1% sulfuric acid to transfer the precipitate to the filter. Place a 150-ml. beaker under the funnel, puncture the paper, and wash through most of the tungstic acid with water. Dissolve the remainder of the material on the filter with hot 4% sodium hydroxide Add 5 to 10 ml. more to the original beaker to dissolve any precipitate that adheres to the glass, using only about 15 ml. in all. It is convenient to have on hand a stock solution of ferric ammonium alum (345 g. of the salt per liter) of such strength that 25 ml. of the solution will contain 1 g. of iron and 1 ml. of sulfuric acid, sp.gr. 1.83. To the main filtrate from the tungstic acid, contained in a 600-ml. beaker, add 75 ml. of this stock alum solution (equivalent to 3 g. of iron) and, stirring constantly, pour in the sodium tungstate which will contain some ferric hydroxide in suspension. A

[18] Willard and Young, Ind. Eng. Chem., **20**, 764, 769 (1928).

clear solution will result, and the volume of liquid at this point should be about 200 ml. Add 6 ml. of hydrochloric acid, sp.gr. 1.18, if a 1.5 g. sample of steel was used, or 4 ml. if a larger sample than 2 g. was taken, and 1.5 to 2 g. of potassium bromate. From this point the procedure is as given in the preceding section.

NOTE.—If undecomposed carbides are found in the foregoing procedure, the tungstic acid may be fused with sodium peroxide in an iron crucible. After extracting with water and decomposing excess peroxide, and addition of 0.1 g. of sodium sulfite to reduce any chromate present, the solution may be returned to the main filtrate to which additional iron has been added.

Purity of Bromate.—Chlorate is frequently present; by blank tests it was found that as much as 0.12% is not harmful; 0.25% of potassium chlorate, however, caused a blank correction of 0.12 to 0.15 mg. vanadium. Test of bromate: add to 200 ml. of water in a 600-ml. beaker, 3 ml. concentrated sulfuric acid, sp.gr. 1.83, 6 ml. hydrochloric acid, sp.gr. 1.18, 5 g. of ammonium sulfate, and 2 g. of the bromate. Boil 10 minutes and cool to room temperature. If not more than 3 drops (0.22 ml.) of methyl orange (0.02 g. indicator in 100 ml.) will impart a permanent color to this solution, the material is satisfactory for the bromate oxidation method.

Chromium plus Vanadium in Chrome-Vanadium-Tungsten Steels.—A 1 to 1.5 g. sample is convenient. Place it in a 400-ml. beaker, add 40 ml. of water and 10 ml. sulfuric acid of sp.gr. 1.83. Warm gently until there is no further evolution of hydrogen. Boil over a free flame until salts begin to separate in order to assist in breaking up carbides, dilute to about 50 ml. and heat until the salts have dissolved. To the boiling hot solution add nitric acid, sp.gr. 1.42, drop by drop, until the violent action is over, then 5 to 6 ml. in excess. Boil down until the tungstic acid separates in considerable amount; dilute to 60 to 70 ml. with hot water, let settle, and filter off the tungstic acid, using 1% sulfuric acid to transfer the precipitate to the filter. Place a 150-ml. beaker under the funnel, puncture the paper, and wash through most of the tungstic acid with water. Dissolve the remainder of the material on the filter with hot 4% sodium hydroxide. Add 5 to 10 ml. more to the original beaker using only about 15 ml. in all. To the main filtrate from the tungstic acid, contained in a 600-ml. beaker, add 1 g. of iron in the form of stock ferric alum solution (see preceding procedure), and, stirring constantly, pour in the sodium tungstate solution. A clear solution will result and the liquid should be diluted at this point to 300 ml. Heat to boiling, add 10 ml. of silver nitrate containing 2.5 g. of $AgNO_3$ per liter, and 5 g. of ammonium persulfate. If no permanganate tinge appears in the solution on boiling, a little more persulfate must be added. Boil the solution 10 minutes to decompose excess of persulfate. Add 5 ml. of 1 : 3 hydrochloric acid to reduce permanganate, and boil vigorously for 10 minutes to remove chlorine. Cool in ice to 5° C., add 25 ml. of ice-cold sulfuric acid, sp.gr. 1.5, and titrate electrometrically with 0.1 N ferrous sulfate.

Chromium plus Vanadium in Chrome-Vanadium Steels.—A 2 g. sample is convenient when the steel contains not more than 2% chromium; for samples of larger chromium content a 1 g. sample is suitable. Place it in a 600-ml. beaker, and dissolve as directed in the preceding procedure. After completion of solution and treatment with nitric acid, and expulsion of oxides of nitrogen, the

solution is diluted to 300 ml. and oxidized with persulfate in the presence of silver nitrate, etc., exactly as described in the preceding section.

If no vanadium is present, the latter two procedures give chromium alone. If both chromium and vanadium are present, the vanadium alone is determined by the bromate oxidation procedure, and hence the amount of chromium can be determined by difference after the determination of the sum of chromium and vanadium by the appropriate one of the latter procedures.

Simplified Titration Methods

Thus far we have considered in detail only the classical potentiometric method, using indicator and reference electrodes. Mention has been made of the Kelley single deflection end-point (p. 2315). Still simpler procedures are possible.

Pinkhof-Treadwell Method.[19]—The titration cell consists of the usual indicator electrode, and a specially constructed reference electrode which has the single potential that the indicator electrode will assume at the end-point. For example, a silver-silver chloride electrode covered with a sodium nitrate solution might serve in titrating chloride with silver, or vice versa. No potentiometer or external source of current is needed. The two electrodes (silver wire, and silver-silver chloride half cell) are joined in series with a tapping key, resistance, and galvanometer. At the end-point the galvanometer shows zero deflection, and the direction of the deflection reverses as the end-point is passed. Müller made this procedure general by the device of opposing an E.M.F. equal and opposite to that known to be developed by the usual indicator-reference electrode system at the end-point.

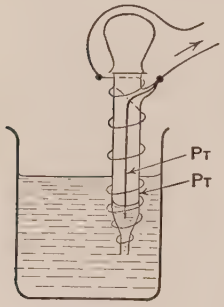

Fig. 333.—Differential Apparatus. Constructed from a medicine dropper and two platinum wires. After each reading near the end-point the sheltered portion is forced into the solution by squeezing the bulb.

The Differential Method.—If one of two similar metal electrodes is sheltered by some device that withholds a small part of the solution from mixture with the remainder, then with small additions of reagent near the end-point, followed by allowing the sheltered portion of the solution to mix with the rest, the differences in E.M.F. between electrodes plotted against small increments of reagent gives a sharp maximum at the end-point.[20] The extremely simple electrode system of Hall, Jensen and Bäckström is shown in Fig. 333, and the more elaborate ones of MacInnes and Dole, and of Clarke and Wooten are represented in Fig. 334. The

[19] J. Pinkhof, Dissertation, Amsterdam, 1919. Treadwell and Weiss, Helv. Chim. Acta, **2**, 680 (1919).

[20] Cox, J. Am. Chem. Soc., **47**, 2138 (1925); MacInnes and Jones, ibid., **48**, 2831 (1926); MacInnes and Cowperthwaite, ibid., **53**, 555 (1931); MacInnes and Dole, ibid., **51**, 1119 (1929); Roth, Z. Elektrochem., **33**, 127 (1927); Heckzo, Z. analyt. Chem., **73**, 404 (1928); **74**, 289 (1928); **75**, 183 (1928); Kamienski, Bull. Acad. Polonaise des Sci. et Lettres, p. 33 (1928); Müller and Kogert, Z. physik. Chem., **136**, 448 (1928); Hall, Jensen and Bäckström, J. Am. Chem. Soc., **50**, 2217 (1928); Clarke and Wooten, J. Phys. Chem., **33**, 1468 (1929); Shukoff and Gortikoff, Z. Elektrochem., **35**, 853 (1929); Rabinovich, Z. Elektrochem., **34**, 311 (1928).

latter (Fig. 334, (2)) made possible the titration of 0.001 N acetic acid with equivalent baryta solution with a mean deviation of $\pm 0.8\%$, using quinhydrone

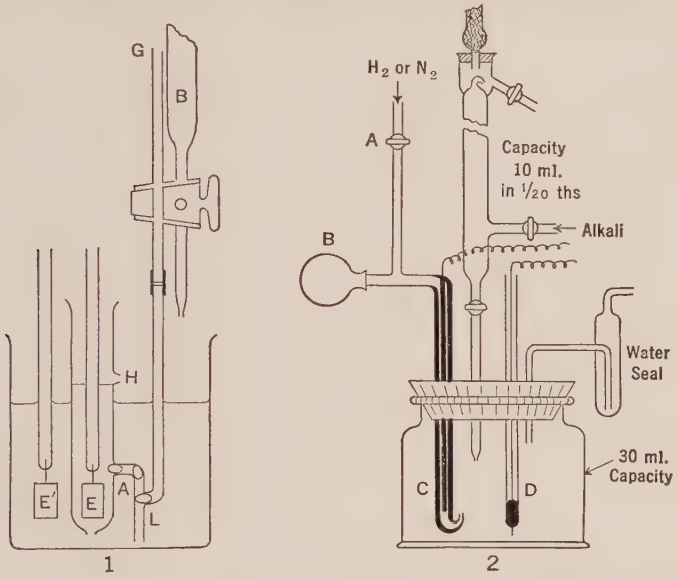

Fig. 334.—Differential Apparatus. (1) MacInnes and Dole's apparatus. Inert gas passes through *G*, and operates the lift pump, *L*. The bottom hole of tube *A* is of capillary dimensions; opening, *H*, is a safety outlet which functions when the pump operates too rapidly. (2) Apparatus of Clarke and Wooten. *C* is a sheltered electrode. When tap *A* is closed, the solution about the sheltered electrode may be pumped into the main solution by means of the rubber bulb, *B*.

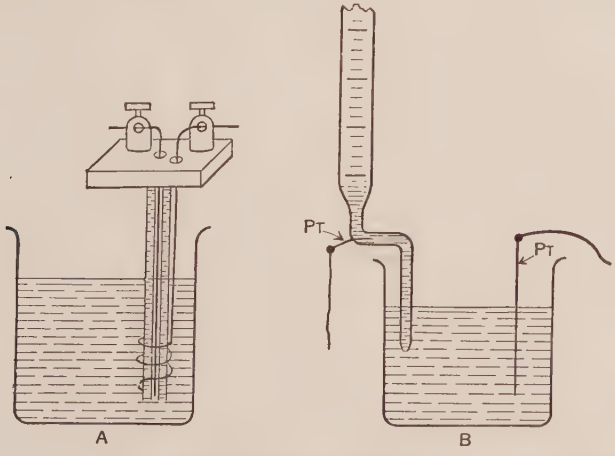

Fig. 335.—A. Müller's Capillary Reference Electrode. So little liquid remains in the capillary that no correction need be applied in ordinary work. *B*. Burette electrode of Willard and Boldyreff.

electrodes. MacInnes and Dole have shown that great precision ($\pm 0.003\%$) may be obtained in the differential method as applied to argentometric titration.

Closely allied to the simplified differential method are the capillary electrode of Müller,[21] Fig. 335*A*, and the burette electrode, Fig. 335*B*, of Willard and Boldyreff.[22] These devices do not, however, give differential readings, but rather the customary form of titration graph which has a maximum jump in potential at the end-point.

Bimetallic Electrodes. (*a*) ***Dissimilar Electrodes.***—A number of studies have been made of the use of pairs of metallic electrodes in neutralizations.[23] A large number of possible electrode pairs have been studied; the most satisfactory, according to Holt and Kahlenberg are tungsten-natural graphite, antimony-natural graphite, and tungsten-silver. These pairs were applied in the titration of 0.1 N acids with 0.1 N bases.

The application of dissimilar metallic electrodes in the field of *oxidation-reduction* reactions is largely the work of Willard and Fenwick.[24] They found that a system composed of platinum, or platinum-rhodium, with tungsten gave excellent results. There is a sharp break in the E.M.F. vs. ml. curve at the end-point. After the break the two electrodes may stay at different potentials, or come together, depending upon the nature of the reaction. Furman and Wilson [25] found that the platinum-tungsten system if joined in series with a high resistance and a galvanometer, gave a maximum galvanometer deflection at the end-points of many oxidation-reduction reactions (Fig. 336).

Polarized Systems.—If two platinum electrodes, as nearly as possible identical, are polarized with a very small current, then at the end-points of

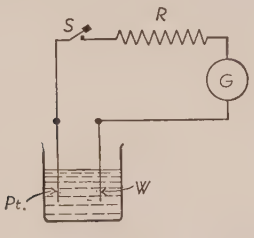

Fig. 336.—Furman and Wilson's Apparatus. The less sensitive the galvanometer, *G*, the smaller the resistance, *R*, which is a radio grid leak. For a galvanometer of 0.05 microamp. sensitivity, *R* should be about 1 megohm.

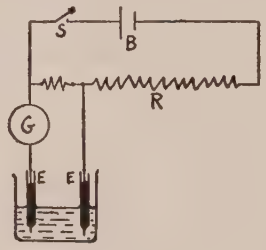

Fig. 337.—Foulk and Bawden Apparatus. *E*, *E*, electrodes; *B*, dry cell, *S*, switch, *R*, resistance (the resistance between the electrodes must be a small portion of the total). *G* is a lamp and scale galvanometer of about 0.05 microampere per mm. sensitivity.

[21] Müller, Z. physik. Chem., **135**, 102 (1928).
[22] Willard and Boldyreff, J. Am. Chem. Soc., **51**, 471 (1929).
[23] Brünnich, Ind. Eng. Chem., **17**, 631 (1925); Fuoss, Ind. Eng. Chem., Analyt. Ed., **1**, 125 (1929); Kahlenberg and Krueger, Trans. Am. Electrochem. Soc., **56**, 201 (1929); Holt and Kahlenberg, ibid., **57**, 361 (1930).
[24] Willard and Fenwick, J. Am. Chem. Soc., **44**, 2504 (1922); Fenwick, Dissertation, University of Michigan, 1922; Hostetter and Roberts, J. Am. Chem. Soc., **41**, 1337 (1919); VanName and Fenwick, J. Am. Chem. Soc., **47**, 9 (1925).
[25] Furman and Wilson, J. Am. Chem. Soc., **50**, 277 (1928).

oxidation-reduction reactions there is a sudden depolarization phenomenon, and the electrode pair suddenly develops a large difference in potential (100 to 200 millivolts).[26] This gives a sharp indication of the end-point which is limited to a small volume of standard solution, and hence the end-point may be over-stepped. Foulk and Bawden [27] have devised a simple continuous-reading

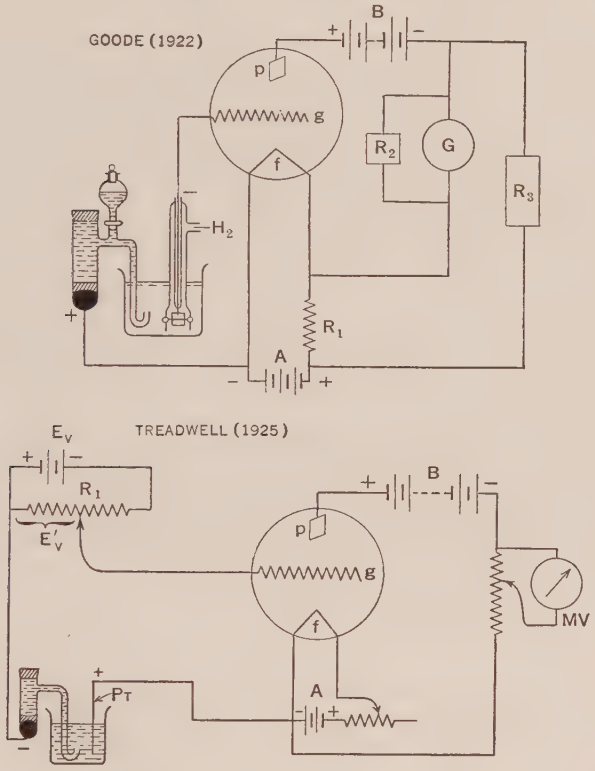

FIG. 338.—Thermionic Vacuum Tube Circuits. (1) Goode's circuit. R_3 serves to balance out the residual plate current, and resistance R_2 serves as a shunt for the galvanometer. (2) Treadwell circuit. A small voltage is put in series with the titration cell to operate on a favorable portion of the plate current-grid voltage line. The indicating instrument is a millivoltmeter of the kind used in thermocouple work.

system with polarized platinum electrodes (Fig. 337). The end-point is a sudden shift of the galvanometer needle either from zero to a large deflection or vice versa, after which it assumes a stationary position; it is, therefore, called the "dead-stop" end-point.

Use of Vacuum-Tube Voltmeters.—The titration cell may be bridged between the negative end of the filament circuit in such a way that the negative

[26] Willard and Fenwick, J. Am. Chem. Soc., **44**, 2516 (1922); VanName and Fenwick, ibid., **47**, 19 (1925).

[27] Foulk and Bawden, J. Am. Chem. Soc., **48**, 2044 (1926).

end of the titration cell is attached to the grid of the radio tube. A sensitive milliammeter, millivoltmeter, or galvanometer in the plate circuit then gives readings that are proportional to the E.M.F. of the titration cell, if the conditions are such that the plate current is a linear function of the grid voltage.[28] Diagrams of two simple circuits are shown in Fig. 338. The circuit described by Treadwell (Fig. 338 (2)), is easy to construct and operate. For industrial use at intervals over long periods of time it is desirable to have a rugged switchboard type of milliammeter, range 0 to 0.5 milliamp. as indicating instrument, and a "B" battery of small lead storage units (cf. Ehrhardt, loc. cit.). Many commercial vacuum-tube voltmeters are now available. They have the advantage of compact construction, since batteries are eliminated by the use of a "power-pack" which enables one to plug the instrument into the A.C. lighting circuit and make continuous-reading titrations.[29]

Micro-methods.—The potentiometric method offers certain advantages in micro determinations, particularly in oxidation-reduction methods, and in certain precipitation processes.[30]

[28] Goode, J. Am. Chem. Soc., **44**, 26 (1922); **47**, 2483 (1925); J. Opt. Sci. Rev. Sci. Insts., **17**, 59 (1928); Calhane and Cushing, Ind. Eng. Chem., **15**, 1118 (1923); Treadwell, Helv. Chim. Acta, **8**, 89 (1925); Bienfait, Rec. Trav. Chim., **45**, 166 (1926); Ehrhardt, "Chem. Fabrik," pp. 443, 455, 463 (1929); Gelbach and Compton, Ind. Eng. Chem., Analyt. Ed., **2**, 396 (1930).

[29] Some typical circuits and further literature references are given by: Partridge, J. Am. Chem. Soc., **51**, 1 (1929); Fr. Müller, Trans. Electrochem. Soc., **62**, 335 (1932); Compton and Haring, ibid., **62**, 195 (1932); Willard and Hager, Ind. Eng. Chem., Anal. Ed., **8**, 144 (1936); Garman and Droz, ibid., **1**, 341 (1935).

[30] Nussberger, Dissertation, Zürich, 1924, p. 40; Benedetti-Pichler, Z. analyt. Chem., **73**, 200 (1928); Niederl and Müller, J. Am. Chem. Soc., **51**, 1356 (1929); Zintl and Betz, Z. analyt. Chem., **74**, 330 (1928).

CONDUCTOMETRIC METHODS[1]

1. THE PRINCIPLES OF CONDUCTOMETRIC TITRATIONS

Electrometric titrations can be divided into two groups: potentiometric methods, discussed in a previous chapter, and conductometric procedures. The theory underlying these two groups is entirely different. The theory of potentiometric titrations as has been pointed out is very similar to that of ordinary titrations, insofar as the change of the potential of a suitable electrode is a linear function of the change of the logarithm of the ion concentration or the logarithm of the ratio of concentration of oxidant to reductant in the system to be titrated. A large jump in potential at the equivalence point means a sharp color change of a suitable indicator; and the titration to a definite potential is comparable with an ordinary titration in which the reagent is added until the indicator has assumed a definite color. Therefore, the electrode in a potentiometric titration can be more or less compared to a specific indicator for the ion or redox system to be titrated.

In conductometric work, on the other hand, all ions present contribute to the electrical conductivity of the solution. If an electrolyte is added to a solution of another electrolyte without changing the volume to any appreciable extent, the conductivity increases insofar as the electrolytes do not react with each other. If an ion of one electrolyte unites with an ion of the other to form a slightly dissociated or slightly soluble substance or if it changes the total ion concentration by an oxidation or reduction process, then the conductivity of the solution may change in three different ways, before the equivalence point has been reached: (1) The conductance decreases. (2) The conductance remains unchanged. (3) The conductance increases.

The conductance of various ions for the electric current is different. It is usually expressed by the mobility of the ion. The equivalent conductivity Λ of an electrolyte BA is equal to the sum of the mobilities of both ions:

$$\Lambda_{BA} = \lambda_{B^+} + \lambda_{A^-}.$$

The equivalent conductance Λ is the conductance in reciprocal ohms of a solution containing one gram equivalent of solute when placed between electrodes which are one cm. apart; hence, it is equal to the specific conductance divided by the concentration, the latter being expressed in equivalents per ml.

$$\Lambda = \frac{\kappa}{C} 1000.$$

κ denotes the specific conductance of the solution, c the concentration expressed in equivalents per liter. The equivalent conductance in other words is the specific conductance the solution would have if the electrolyte were present in a concentration of one equivalent per ml. On account of the interionic effect the equivalent conductance or the mobility of the ions decreases

[1] By I. M. Kolthoff, Professor of Chemistry, University of Minnesota.

with increasing electrolyte content of the solution. The values reach a maximum at infinite dilution. In dilute solutions the following relation holds between the equivalent conductance Λ_c at a concentration c and Λ_∞:

$$\Lambda_c = \Lambda_\infty - A\sqrt{c}.$$

A is a constant which is different for various electrolytes. The mobility of the ions increases very much with the temperature, as their migration velocity increases. The increase of the mobility of most ions is 2 to 2.5% for 1° C. increase in temperature, for hydrogen ions the change is only 1.5% for hydroxyl ions 1.8% per one centigrade degree change in temperature.

In the following table the mobility of some ions at 25° and at infinite dilution are reported. The data are taken from reliable studies reported in the literature.

Mobility of Some Ions at 25° at Infinite Dilution

Li^+	41.7	OH^-	193
Na^+	50.8		
Ag^+	63.4	Cl^-	75.8
K^+	74.8	NO_3^-	70.9
NH_4^+	74.9	HCO_3^-	47
H^+	350	IO_3^-	39.6
		CH_3COO^-	40.8
$\frac{1}{2}Ba^{++}$	65.2	$\frac{1}{2}CO_3^=$	70
$\frac{1}{2}Ca^{++}$	61	$\frac{1}{2}C_2O_4^=$	73.5
$\frac{1}{2}Mg^{++}$	55.0	$\frac{1}{2}SO_4^=$	80.0
$\frac{1}{2}Pb^{++}$	71.0	$\frac{1}{3}Fe(CN)_6^{\equiv}$	97.3
Tl^+	76.0	$\frac{1}{4}Fe(CN)_6^{\equiv}$	100.8
$\frac{1}{2}Ni^{++}$	53.6		
$\frac{1}{2}Fe^{++}$	54		
$\frac{1}{3}Fe^{+++}$	68.4		

Let us now consider how the conductance of a solution of a strong electrolyte BA will change upon the addition of a reagent CD, assuming that the cation B^+ reacts with the anion D^- of the reagent. If the product of reaction is slightly dissociated or insoluble, the reaction may be expressed by the equation:

$$\underset{\text{Ion to be determined}}{B^+} + A^- + \underset{\text{reagent}}{C^+ + D^-} \rightarrow \underset{\text{insoluble or slightly dissociated.}}{BD} + A^- + C^-$$

Therefore, by the reaction between B^+ and D^- ions, the B ions during the titration are replaced by C ions.

Case 1.—The mobility of the B ions (λ_B) is greater than λ_C: the conductance of the BA solution decreases upon the addition of the reagent CD. This case generally occurs in the titration of strong acid with strong bases or in the reverse titration. The hydrogen and hydroxyl ions distinguish themselves from the other ions by a much larger mobility. (See table, above.)

Case 2.—λ_B and λ_C are equal. The conductance remains unchanged by the addition of CD until the equivalence point has been reached. This case is met with in most precipitation reactions. In the titration of silver nitrate with barium chloride, the barium ion takes the place of the silver ion and as both ions have about the same mobility, the conductivity does not change during the

reaction. If instead of barium chloride, sodium chloride is used as a reagent, the conductivity decreases slightly as λ_{Ag^+} is greater than λ_{Na^+}. On the other hand with potassium chloride as a reagent, the conductivity increases slightly because λ_{Ag^+} is smaller than λ_{K^+}.

Case 3.—The conductivity increases from the beginning of the titration if a slightly dissociated substance is titrated and the reaction product is a strong electrolyte. This case in general occurs in the neutralization of a weak acid with a strong base or a weak base with a strong acid. In any case the conductivity increases after the equivalence point has been reached, at least if the reagent is a strong electrolyte.

In a conductometric titration the conductance is measured after addition of successive amounts of reagent. The points thus obtained are plotted to give a graph which as a rule consists of two straight lines intersecting at the equivalence point. Therefore, the latter is found in a graphical way. In contrast to any other type of titration method, measurements near the equivalence point have no special significance. As a matter of fact the values found near the equivalence point are often worthless in the construction of the two straight lines, on account of the fact that the reaction product by its dissociation or solubility contributes to the conductivity of the solution whereas we have to know the data where the conductivity caused by the reaction product itself is negligibly small. In reactions which can be made the basis of a conductometric titration, the latter is always the case, when there is an excess of ion to be titrated or reagent. Near the equivalence point the points often do not lie on one of the two straight lines, but the conductivity found is higher than the corresponding ones on the straight lines (titration of very weak acids and bases; hydrolysis; precipitation reactions); comp. Figs. 346, 347, and 348.

The point mentioned that a marked hydrolysis, solubility or dissociation of the reaction product does not affect the accuracy of the method very much makes the application of *conductometric titrations possible to those cases where other titration methods fail to give results.* This will be shown by several examples in the following review.

On the other hand, it is emphasized here that the conductometric method can be much less generally applied than the ordinary or potentiometric one, on account of the fact that large amounts of foreign electrolytes which do not take part in the reaction, affect the accuracy greatly. The relative change of the conductivity during the reaction and upon addition of excess of reagent mainly determines the accuracy and this change is decreased by the presence of foreign electrolytes. Of course one must not infer from this that the conductometric method is rendered impossible by the presence of foreign electrolytes; if precision methods are used in the measurement of the conductivity and the titration is carried out in a thermostat, the method can be applied in the presence of relatively large amounts of indifferent electrolytes. This, however, is reached at the cost of the simplicity of the method.

2. THE PERFORMANCE OF CONDUCTOMETRIC TITRATIONS

For details about the measurement of electrical conductance and the significance of the cell constant the reader is referred to textbooks on electrochemistry.

An ordinary conductometric titration can be carried out in a relatively short time (ten minutes or longer).

A titration cell as given in Figs. 339 or 340 can be used. Figure 339 gives the more or less classical model of Dutoit. The two platinized platinum electrodes are in a vertical position in order to prevent the deposit of a precipitate in precipitation reactions. The electrodes are welded to a platinum wire, the latter being sealed in the glass and making electrolytic contact outside the vessel in a mercury pocket. The cell is placed in a block of wood or paraffin. Successive portions of the reagent are added from a microburet which can be connected in some way to a reservoir containing a supply of the standard solution. It is recommended to use a reagent which is at least ten to twenty times more concentrated than the solution to be titrated. The cell in Fig. 339 also contains a thermometer divided into 0.1 degrees. A change in temperature during the titration will effect the result very much as the conductivity increases greatly with increasing temperature (for most salts about 2 to 2.5% for 1°). In cases where the heat of reaction is fairly high, irregularities in the conductivity curve may occur on account of the temperature effect. As a rule, however, the heat effect during a titration is very small. After the addition of reagent the cell is shaken to secure homogeneous mixing; in this manipulation one has to be careful not to warm the solution by taking the whole cell in his hand. Convenient for the shaking is a glass handle attached to the cell as in Fig. 340. If work is done with solutions of quite different conductance, one should have a few titration cells with different cell constants adapted to the special work. The accuracy in the location of the end-point in conductometric titrations as a rule is not larger than 0.5 to 1%. For precise work it is recommended that the titration be performed in a thermostat.

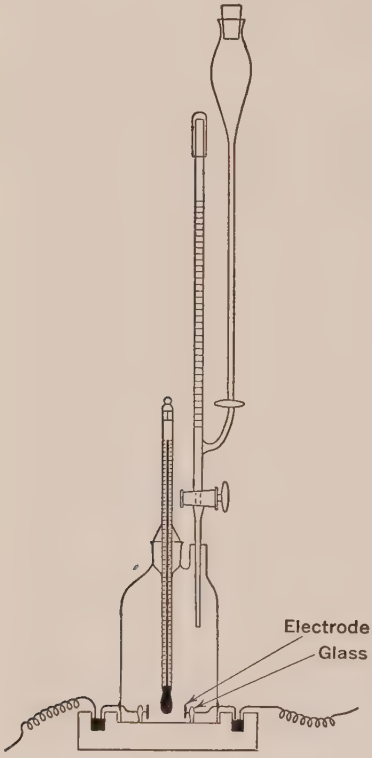

Fig. 339.

It is not necessary to know the absolute values of the specific conductivity of the solution during the titration; the reciprocal value of the resistance can be plotted as it is proportional to the conductance.

The conductance can be measured according to the classical method of the Wheatstone bridge, using a telephone for the detection of the minimum. Though this method is quite satisfactory, it has a special disadvantage, namely, that one needs a quiet room, undisturbed by noises. This requirement might prevent a more general application of conductometric titrations. Fortunately,

at the present time the telephone can be replaced by other instruments or arrangements so that the minimum can be detected in a visual way.

In the first place the Leeds and Northrup alternating current galvanometer may be mentioned. The equipment provides means for utilizing current from a sixty cycle 110 volt A.C. circuit and the galvanometer is especially recommended for conductometric titration work. It is not suitable for highly precise measurements and even in titrations some difficulties may arise by polarization of the electrodes and the heating of the solution in the cell. If these difficulties are overcome, it seems that the A.C. galvanometer will furnish us with the simplest apparatus for detection of the point of balance on the Wheatstone bridge. Of other methods recommended, those advocated by G. Jander and O. Pfundt [2] will be briefly discussed. They use a thermo-cross (Fig. 341) or a special commutator (crystal detector) (Fig. 342 as rectifiers. In Fig. 341 the thermo-cross, *Th*, and the transformers are placed in the Wheatstone bridge instead of the telephone. The thermo-cross consists of a couple of constantan

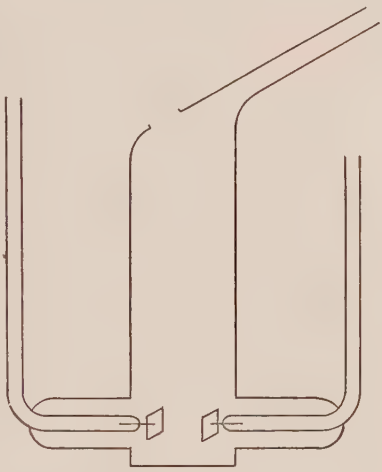

FIG. 340.

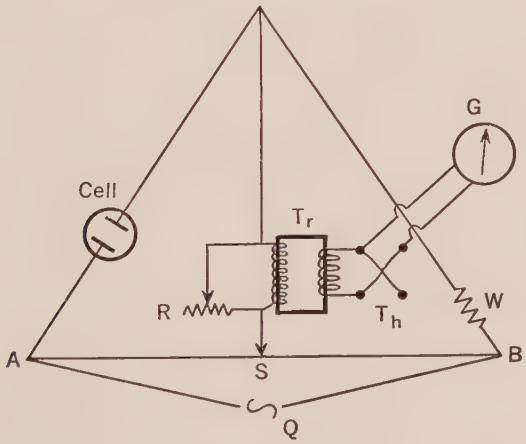

FIG. 341.

and iron wire kept in a small box to protect it from atmospheric disturbances. If a current passes through the bridge a thermo current is developed and the

[2] G. Jander and O. Pfundt, "Die visuelle Leitfähigkeitstitration," 2d Ed., Stuttgart 1934, Verlag Enke, also in "Physikalische Methoden der Analglischen Chemie," Akad. Verlagsges. Leipzig, 1936, pp. 1–54.

galvanometer G gives a deflection. In order to prevent the direct current from passing through the conductivity cell, the transformer, T, is placed in the circuit. R is a resistance by means of which the sensitivity of the system can be regulated. W is a known resistance and AB a slide wire used as in the ordinary method. The apparatus can be used in different ways; many details have to be considered, for which the reader is referred to the work of Jander and Pfundt. Simpler to manipulate is the system in Fig. 342 where U represents the rectifier. It may be mentioned that T. Callan and S. Horrobin [3] a few years ago described a similar arrangement in which they used a carborundum detector (from the Carborundum Company) as a rectifier, also W. D. Treadwell and S. Janett [4] made use of a commutating device to avoid the use of the telephone.

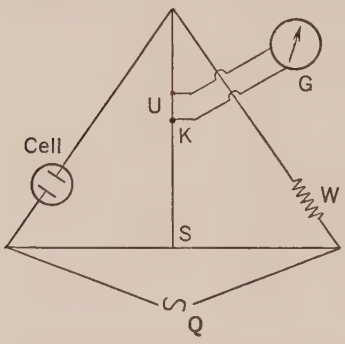

Fig. 342.

3. APPLICATION OF CONDUCTOMETRIC TITRATIONS TO ACID–BASE REACTIONS

In this paragraph a condensed review of the application of conductometric titrations to acid-base reactions will be given. For details the reader is referred to a monograph of I. M. Kolthoff.[5]

Strong Acids with Strong Bases.—In the following graphs the ordinate represents the conductivity and the abscissa the volume of reagent added. In the titration of a strong acid with a strong base (or vice versa) a sharp break in the conductivity occurs at the equivalence point. Theoretically the minimum should not occur exactly at the equivalence point where pH is 7, but slightly at the alkaline side as the mobility of the hydrogen ions is much larger than that of the hydroxyl ions. From a simple differential equation it can be computed that the minimum occurs at a hydroxyl ion concentration of 1.4×10^{-7}. The difference between this and the neutral point is so small that it cannot be determined experimentally.

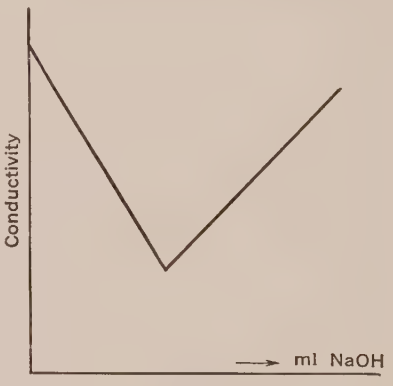

Fig. 343.

It is of interest to note that the shape of the conductivity line is independent

[3] T. Callan and S. Horrobin, J. Soc. Chem. Ind., **47**, T329 (1938). Compare also H. T. S. Britton, "Conductometric Analysis," D. Van Nostrand Company, Inc., New York, 1934.

[4] W. D. Treadwell and S. Janett, Helv. chim. act., **6**, 734 (1923).

[5] I. M. Kolthoff, "Konduktometrische Titrationen," Dresden, 1923, Verlag Steinkopff.

of the dilution. Extremely dilute solutions of strong acids or strong bases, of the order of 0.0001 N, can be titrated with the same accuracy as more concentrated solutions if care is taken to exclude carbon dioxide.

On the whole, the application of the conductometric titration in this case has only practical significance when the solution has a dark color so that the indicator method fails to give results.

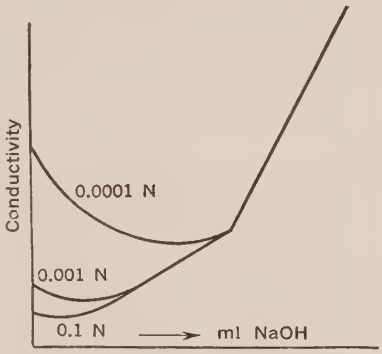

Fig. 344.

Intermediate Weak Acids and Bases.—The shape of the neutralization curve depends upon the concentration and the ionization constant of the acid or base. By neutralization of the dissociated part of the acid, the conductivity will drop and on account of the formation of its salt which behaves as a strong electrolyte, the conductance increases. The practical neutralization curve is obtained by adding the figures of the "acid-depression curve" to those of the "salt line." The more strongly the acid is ionized, the more its neutralization curve approaches that of a strong acid and the less it is ionized the more it behaves like an extremely weak acid; the latter case will be discussed later.

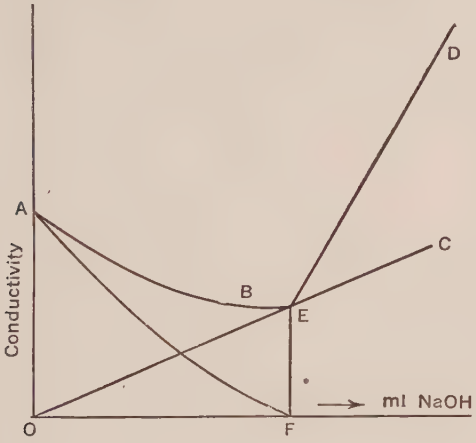

Fig. 345.

ABE—Neutralization Curve.
ED—Sodium Hydroxide Curve
OEC—Salt Line.
AF—Acid Depression Curve.

In Fig. 344 the neutralization curves are given for the neutralization of 0.1 N, 0.001 N and 0.0001 N acetic acid, respectively. From the above it is evident that in many cases a flat minimum will occur in the neutralization curve. Its location can be calculated from the ionization constant, the concentration and the mobilities of the ions present in the system. The minimum itself has no analytical significance though it may give us an indication of the magnitude of the ionization constant of an acid which may be of importance in unknown cases. If the acid is relatively highly ionized, the neutralization line will give a curve up to the equivalence point and it is hard to find with any degree of accuracy the point of intersection of the neutralization curve with the sodium hydroxide line, the latter being the straight line found after addition of an excess of base.

Such a case occurs, for example, in the neutralization of 0.01 N salicylic acid as is shown in Fig. 345. An analysis of the curve shows that the equivalence

point is found at the point of intersection of the salt line and sodium hydroxide line. The former can be determined in an experimental way. Suppose 100 ml., 0.01 N salicylic acid are titrated with 0.5 N sodium hydroxide so that the sodium hydroxide line can be drawn. In order to find the shape of the salt line a second determination is made in which 100 ml. of water instead of dilute acid is taken and successive amounts of 0.5 N sodium salicylate of exactly the same strength as the sodium hydroxide are added. From the latter data, the salt line can be constructed and the equivalence point can be found with an accuracy of at least 1%.

If the dissociation of the acid during the neutralization is less than in the above case, the last part of the neutralization curve before the equivalence point will be a straight line. Under these conditions, the point of intersection can be found by a single titration. This is the case, if the ionization constant of the acid is smaller than about 5×10^{-4} in the titration of 0.1 N solutions, smaller than 5×10^{-5} for 0.01 N solutions and smaller than 5×10^{-6} for 0.001 N solutions.

Very Weak Acids and Bases.—The initial conductivity is very small and during the neutralization, the conductivity increases according to the salt line. On account of the hydrolysis of the salt formed, the experimental data near the equivalence point are higher than the corresponding points on the salt and sodium hydroxide line; therefore, in the construction of the two lines, points should be taken at such a distance from the equivalence point that the hydrol-

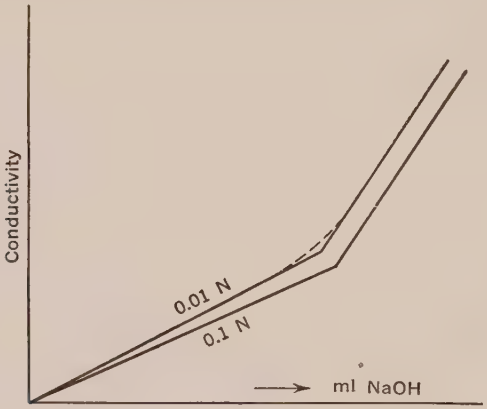

Fig. 346.

ysis is negligibly small and the points can then be combined to give straight lines. If the acid is extremely weak (e.g. hydrogen peroxide) the hydrolysis is so large that the titration does not yield useful results. For the titration of 0.1 N solutions, the ionization constant should be larger than about 10^{-10}, for 0.01 N solutions larger than 10^{-9}, for 0.001 N solutions larger than 10^{-8}. These figures have no exact significance; they only give the order of magnitude of the ionization constant at which useful results can still be obtained.

From the above we see that the conductometric titration can be applied where the potentiometric or ordinary method does not give satisfactory results.

In Fig. 346 neutralization curves of 0.1 N and 0.01 N boric acid with sodium hydroxide are given. Several applications can be made. Hydroxy benzenes, like phenol and resorcinol can be titrated very nicely. A systematic study has shown that resorcinol and hydroquinol behave like dibasic acids, pyrocatechol on the other hand as a monobasic acid. The trivalent phenols, pyrogallol and phlorglucinol behave like dibasic acids. The method has been applied to the titration of nitrophenols, phenolphthalein and other weak acids whose salts are colored. Phenolphthalein in 50% alcohol behaves like a dibasic acid, a break occurring after the neutralization of the carboxyl and phenol groups. The conductometric method should be very useful to organic chemists in cases where they want to know quantitatively the acid or basic character of a colored substance. It can also be recommended for the determination of the equivalent weight of amino acids and polypeptides and the acid or base combining power of proteins. A practical application of the method can be made in the determination of vanillin in vanillin sugar. The aromatic substance is extracted with alcohol and titrated as a monobasic acid.

What has been said for very weak acids also holds for very weak bases. Aniline, hexamethylenetetramine and pyridine can be titrated accurately with hydrochloric acid.

Neutralization of Weak Acids with Weak Bases.—Though in analytical work one always uses a strong acid or a strong base as a reagent, the above case has practical significance; e.g. when a pure ammonium salt of a weak acid has to be prepared or when a weak acid must be titrated in the presence of an ammonium salt or the salt of another weak base.

Figure 347 gives the titration lines of 0.1 N and 0.01 N acetic acid, respectively with ammonia. The neutralization curve up to the equivalence point is

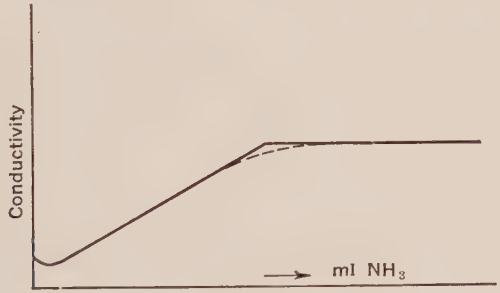

Fig. 347.

about the same as found with sodium hydroxide since both sodium and ammonium acetate are strong electrolytes. After the equivalence point has been reached, an excess of ammonia leaves the conductivity practically unchanged as the dissociation of the weak base is depressed by the presence of the ammonium salt. On account of the hydrolysis, the values near the equivalence point are somewhat lower than the corresponding points on the straight lines. If the acid or base to be titrated is extremely weak (e.g. boric acid with ammonia), no straight lines can be constructed on account of the strong hydrolysis.

Mixtures of a Strong and a Weak Acid.—Here again the conductometric method can be advantageously applied whereas the ordinary or potentiometric method does not yield satisfactory results. The above case is a combination of two which have been discussed before. First, the strong acid is neutralized and the conductivity drops following a straight line. Near the first equivalence point, the weaker acid will be neutralized and the conductivity will soon increase according to the salt line of the weak acid. In Fig. 348, the change in conductivity during the neutralization of a mixture of 10 ml. 0.01 N hydrochloric acid, 10 ml. 0.01 N acetic acid and 10 ml. of water with 1 N sodium hydroxide is given. The case has practical significance; e.g. for the determination of traces of mineral acids in vinegar. Recently the author, in collaboration with Mr. T. Kameda, has made another application for the determination of the purity of sulfonphthaleins. The sulfonic group behaves as a strong acid and is first neutralized; after the first break, the conductivity increases and after neutralization of the phenolic group, a second break occurs.

Fig. 348.

The application of the conductometric method to the titration of a mixture of two weak acids with quite different ionization constants (like acetic and boric acid) does not have much practical significance, for a sharp break never occurs after the neutralization of the stronger acid. The difference in mobility of the anions of the two acids determines the sharpness of the break and as this difference always is very small, the angle between the two salt lines will be very obtuse. Therefore, as a rule, the first equivalence point cannot be found with a high degree of accuracy.

Replacement Titrations.—When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the stronger one and the weak acid itself is liberated in the undissociated form. Similarly, the addition of a strong base replaces the weak base in a salt of the latter.

Many important applications of these replacement reactions can be made to conductometric titrations; especially those cases are important which do not yield successful results with the indicator of potentiometric method.

If, for example, hydrochloric acid is added to a solution of sodium acetate, the acetate is replaced by the chloride ion. The conductivity increases slightly on account of the fact that λ_{Cl^-} is a little greater than $\lambda_{acetate}$. After all the acetic acid has been liberated, continued addition of hydrochloric acid gives rise to a strong increase in conductance. Fig. 349 gives the conductance lines in the titration of 0.01 N sodium acetate with N hydrochloric acid. On account of the dissociation of the acetic acid, the experimental figures near the equivalence point are somewhat higher than the corresponding ones on the straight lines. If the ionization constant of the liberated acid is smaller than

about 5×10^{-5}, 0.01 N solutions of its salt can be titrated accurately. For 0.1 N solutions, the constant may even be as large as 5×10^{-4}. Ethyl alcohol decreases the ionization of weak acids and in the presence of enough alcohol even salts of stronger acids than those indicated can be titrated.

The method furnishes a simple means for the evaluation of salts of weak acids, such as acetates, benzoates, succinates, etc. Similarly, it can be applied to the determination of ammonia in ammonium salts by titration with sodium hydroxide. A rapid determination of the ammonium content of fertilizers can be made in this way.

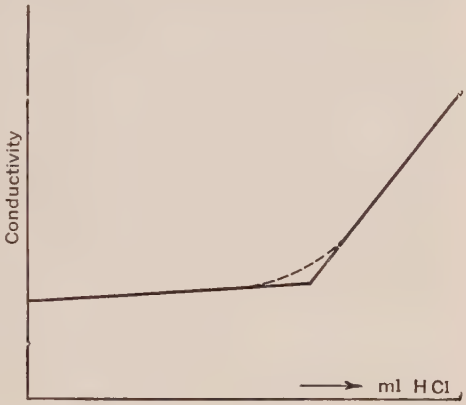

FIG. 349.

In this review, a condensed summary has been given of the application of conductometric titrations to acid-base reactions. For details concerning the combination of different cases and specific cases (carbon dioxide, phosphoric acid, alkaloids, phenols, salts of heavy metals, etc.) the reader is referred to the monograph of Kolthoff (l.c., p. 2328).

From all that has been said, it may be inferred that the significance of conductometric titrations should be more generally recognized. They often furnish us information which could otherwise only be obtained by elaborate work.

4. APPLICATION OF CONDUCTOMETRIC TITRATIONS TO PRECIPITATION AND COMPLEX FORMATION ANALYSIS

A reaction usually can be made the basis of a conductometric titration if the reaction product is a slightly soluble substance or a stable complex. The usefulness and accuracy are mainly dependent upon the following facts:

(*a*) Errors in the determination of the conductance data.
(*b*) Solubility of the precipitate or stability of the complex.
(*c*) Speed of formation of the precipitate.
(*d*) Constant composition (purity) of the precipitate.

(*a*) The same error in the determination may affect the accuracy of the titration in different ways. This depends upon the acuteness of the angle between the precipitation line (line combining the conductance data during the precipitation) and the reagent line (line giving conductance data with excess of reagent). The more acute the angle is the more accurate the result. If the angle is very obtuse, a small error in the conductance data can cause a large deviation. Therefore, one always should endeavor to choose such experimental conditions that the angle is as acute as possible. The following rules should be borne in mind: (1) The smaller the mobility of the ion which replaces the react-

ing ion, the more accurate will be the result. If a silver salt is titrated with lithium chloride, the conductivity decreases during the precipitation and increases after the equivalence point. If hydrochloric acid were used as a reagent, the conductivity would increase from the beginning of the titration and the angle between the precipitation and reagent line would be very obtuse. Therefore, generally it is recommended to titrate cations with lithium salts and anions with acetates. (2) The larger the mobility of the anion of the reagent which reacts with the cations to be determined (or vice versa) the more acute is the angle. For example, it is more advantageous to titrate silver salts with sodium chloride than sodium nitro prusside, as the mobility of the chloride ion is larger than that of the nitro prusside. (3) The titration of a slightly ionized salt does not give good results since the conductivity increases relatively much from the start of the determination. (4) As has been mentioned in the beginning of this chapter, the accuracy of a conductometric titration always suffers from the presence of electrolytes that do not take part in the reaction.

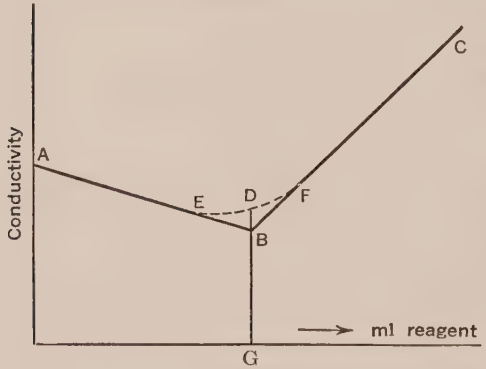

FIG. 350.

(*b*) On account of the solubility of the precipitate, the experimental figures near the equivalence point deviate from the straight line as is shown in Fig. 350. *A E D F C* gives the experimental curve. If the solubility of the precipitate were negligibly small, the conductivity at the equivalence point would be equal to *B G*. By an excess of the ion which is precipitated or an excess of reagent, the solubility is depressed and if the latter is not too large, it usually is possible to construct the precipitation and reagent line by joining points on *A E* and *F C*.

It can be shown that 0.1 N solutions can still be titrated if the solubility of the precipitate formed is less than about 0.005 N (uni-univalent electrolyte); for 0.01 N solutions the solubility should be smaller than about 0.0005 N.

(*c*) The formation of a microcrystalline precipitate is usually a time reaction. After addition of a small amount of reagent, the conductance does not immediately become constant; one must wait for some time. Seeding the solution with the precipitate itself has a favorable effect though in the titration of very dilute solutions even this does not overcome the difficulty. Quite generally it is much better to add enough alcohol to make its concentration about 30–40%. The speed of formation of the precipitate then becomes much larger and furthermore another advantage is gained, the solubility of most slightly soluble substances is materially reduced by alcohol. Of course, one should realize that on addition of alcohol to a solution the temperature rises; therefore, before the titration is started, the mixture should be cooled to room temperature.

(*d*) If the precipitate has strong adsorbent properties, the method does not yield successful results. So, for example, the titration of heavy metals with

sodium sulfide or ferro cyanide cannot be recommended on account of the inconstant composition of the precipitate. If a microcrystalline precipitate like barium sulfate or calcium oxalate is formed, occlusion phenomena may play a part. Finally, it may be mentioned that under certain conditions, the surface conductance of the solid precipitate may affect the results.

Many precipitation or complex reactions have been made the basis of a conductometric titration. A short summary of most satisfactory cases is given below. For details, the reader is referred to Kolthoff's monograph (l.c., p. 2328).

Silver nitrate as a reagent: chloride, bromide, iodide, cyanide, thiocyanate, chromate; molybdate,[6] also iodide in presence of chloride in ammoniacal medium.

Mercuric perchlorate as a reagent (complex formation): chloride, bromide, iodide, cyanide, thiocyanate, formate, acetate and its homologues.

Lead nitrate as a reagent: iodide, ferrocyanide, ferricyanate, sulfate, sulfite, thiosulfate, pyrophosphate, oxalate, tartrate, succinate, benzoate.

Barium acetate (or barium chloride) as reagent: sulfate, chromate, carbonate, pyrophosphate, oxalate, tartrate, citrate.

Sodium perchlorate as reagent: potassium [7] at 0°; it is not accurate, according to the writer's experience.

Lithium sulfate as reagent: barium, strontium calcium, lead.

Sodium chromate as reagent: barium, lead, silver.

Lithium oxalate as reagent: silver, lead, copper, cadmium, nickel, cobalt, manganese, zinc, calcium, barium, strontium, magnesium and strong acids.

Lead acetate as reagent: molybdate, tungstate.[8]

Bismuthylperchlorate as reagent: phosphate.[9]

The author expresses his appreciation to Mr. H. E. Howe, editor of Ind. Eng. Chem. for allowing him to use part of the original manuscript in the preparation of this chapter. Part of this has been published in Ind. Eng. Chem., Anal. Ed , **2**, 225 (1930), and in a monograph entitled "The Colorimetric and Potentiometric Determination of pH. Electrometric Titrations," J. Wiley & Sons, New York, 1931.

[6] C. Candee and I. G. Murgulescu, Bull. Soc. Chim., Romania, **17**, 103 (1935).
[7] G. Jander and O. Pfundt, Z. anal. Chem., **71**, 417 (1927).
[8] E. Rother and G. Jander, Angew. Chem., **43**, 930 (1930).
[9] J. Harms and G. Jander, Angew. Chem., **49**, 106 (1936).

GAS ANALYSIS [1]

SAMPLING

As in all analytical processes, the obtaining of a representative sample is of cardinal importance. It is done by the insertion of a tube into the duct or flue and the withdrawal of the gas into a container. Previous to this, the furnace, duct or setting must be thoroughly inspected for air leaks and these carefully stopped. This is all the more to be done if, as often happens, the boiler plant has been built on filled or " made " land. Finally the fact must not be lost sight of that the bricks themselves composing the setting are porous. The search for leaks is conducted using a lighted candle, and the places where the flame is sucked in are marked and plastered up: the joints in the cleanout doors are often corroded or rusty and no longer fit tightly. This is also true of the frames of the doors themselves in the brickwork. If the bricks and mortar of the setting leak, it should be given a thin coat of size and a couple of coats of thin whitewash to close the pores. Few people have any idea of this loss from air leakage, and by radiation of heat from the setting. A case cited [2] in a western city in which the setting was covered with asbestos cement over which canvas was pasted and the whole heavily painted, showed a saving of 12%.

If the sample be from a boiler it should be taken as soon after leaving it as practicable—not over the grate where the gases might be dissociated, and not at the end of a long duct where they may have been air-diluted. Bends in the ducts should be avoided and a place chosen preferably four or five diameters of the duct away from the bend, where the gases are flowing smoothly. The tube should be inserted to a distance of one-fourth to one-third the radius of the duct from the circumference. Multiple tubes, tubes with varying sized holes, are not to be recommended, as they are of doubtful expediency. Insertion is preferably made on the grate side of the damper, to avoid air leaks, by drilling a hole in the flue and fitting a screwed nipple into the hole: the sampling tube is cemented into this nipple with Portland cement in case of a permanent installation. When the connection is temporary the hole may be puttied or made tight in any way—even with wet cotton waste. A similar hole is made for the thermometer.

a. Tubes.—The best tube is of translucent quartz, about ¼ inch in internal diameter and 3 feet long: this will withstand any temperature or gas likely to be encountered in practice. Pyrex glass tubes will probably be found sufficient for all practical purposes and may be used with temperatures up to 600° C. Uncooled metal tubes cannot be used above 250° as their oxides are reduced by hydrogen and carbon monoxide even at 200° according to the equation $Fe_2O_3 + 3CO = 2Fe + 3CO_2$, the sample will be defective and an utterly false idea obtained of the process by which it was produced. Dust and smoke can be removed by plugs of asbestos, or if the temperature permits, rolls of iron wire gauze or steel wool. These must be replaced when clogged.

[1] Chapter by the late Augustus H. Gill.
[2] Electrical World.

b. Pumps.—Any form of a mechanical pump may be used, of which the ordinary rubber syringe bulb is the simplest. In using this it should be remembered that the valves do not shut tight, and in sampling it may have to be shut off by a pinch-cock. Where a head of water, steam or compressed air is available, the familiar Richards [3] jet pump (Figs. 351 and 352) may be employed. This operates on the principle of the boiler injector—small slugs or pistons of water filling the jet and sucking in the gas after them.

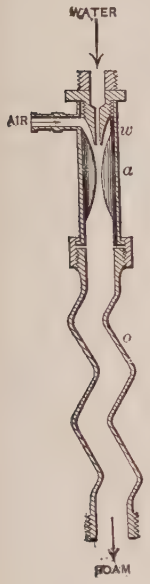

Fig. 351.

Fig. 352.

Where a fall rather than a head of water is available, the Bunsen pump (Fig. 353) is used. This consists of a ¼ inch T connected to the water reservoir and to a 12 ft. piece of ¼ inch rubber tubing *b*, the stem of the T *a* being connected to the source of water. When the water flows it sucks the gas in after it through *c*: 12 ft. of tubing will usually be found sufficient, 34 ft. are needed for the highest vacuum. If none of the foregoing be available, a pair of aspirator bottles described further on may be used.

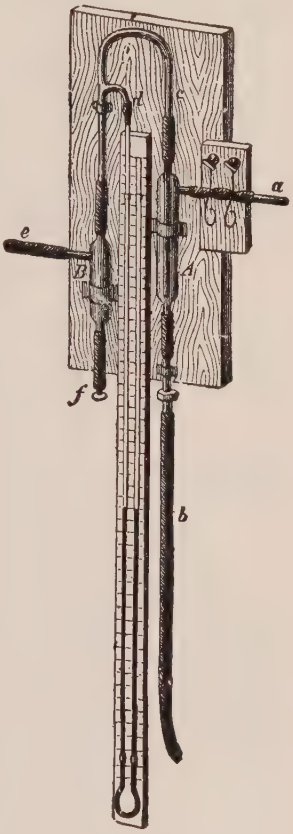

Fig. 353.

c. Containers.—These should be of glass, or a metal which is unacted upon by the gases to be encountered. Rubber bags are unsuitable, for rubber is by no means the inert substance which we are in the habit of considering it. Rubber is oxidized or attacked by various gases and allows the lighter gases to transfuse through it, and dissolves the heavier hydrocarbons, as ethylene. Acid gases like sulfur dioxide are dissolved perceptibly by passing through the usual white laboratory tubing, containing 50 to 60% of zinc oxide, giving low results. In consequence of this, rubber connections exposed to gases in all gas apparatus should be as short as possible, the glass tubes being butted together, leaving barely room for the pinchcock. *The ends of all glass tubes connected by rubber must be file-rounded*, to remove the sharp cutting edge of the glass tubing—a prolific source of leaks in stoppers as well as rubber connectors.

The shape of the container should be such as to allow the water in it to wholly run out; a glass bulb, pear-shaped at the bottom (Fig. 354), is excellent.

[3] Am. J. Sci. (3), **8**, 412 (1874).

If this cannot be had a separatory funnel may be employed. It is used by filling with water, attaching the sampling tube at *i* the pump opposite. Upon pumping, a stream of gas passes through the T from which a sample is taken by allowing the water to run out completely: *h* serves as an attachment for water in dispensing gas from *i* when in the laboratory. The tubing shown in the figure is of lead, which can be safely used for chimney gases after it becomes attacked by them. Its obvious advantage is found in the fact that it bends rather than breaks.

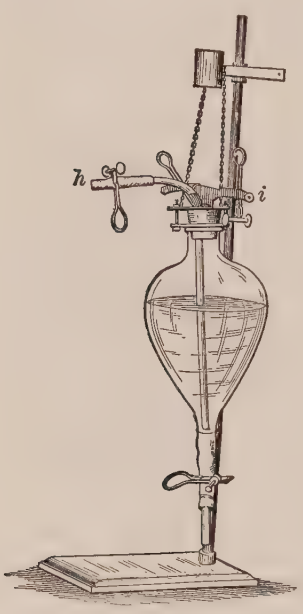

FIG. 354.

A pair of aspirator bottles—Fig. 355—serving both as pump and container will be found useful. These are bottles or glass jugs, each fitted with a right-angled long tube going nearly to the bottom and a similar short tube ending just under the stopper. The long tube at its lower end carries a short piece of rubber tubing, extending to the wall of the bottle. This enables it to be completely emptied of water when tipped. The long tubes are connected by 4–6 feet of ¼ inch rubber tubing with a screw pinchcock upon it. The short tubes carry rubber connectors and pinchcocks completing the apparatus. Upon filling one bottle with water, preferably saturated with the gas, setting it 3 to 4 feet higher than the other and blowing into the short tube, water flows into the long rubber tube sucking air into the bottle after it. The stoppers can be wired in, taking the precaution to put a piece of stiff leather or metal over the top of the stopper: this prevents the rubber stopper from being drawn away from the glass tubing which would give rise to leaks. Before using the bottle into which the sample is to be taken, it must naturally be completely full of water. These can be used for taking continuous samples.

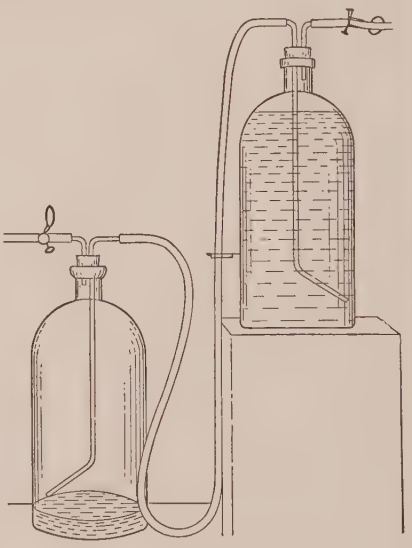
FIG. 355.

For the collection and preservation of small samples, glass tubes or bulbs holding about 100 ml., closed by extra well-fitting stopcocks or which can be sealed off, can advantageously be employed.

As a confining liquid, mercury should be used for results of the highest degree of accuracy—for our purpose it is a super-refinement. Tap water saturated

with the gas sought, is the next best, or tap water alone, or strong brine. In using the latter it should be remembered that it corrodes metal—pinchcocks, etc., and salt is hygroscopic.

In this connection the fact should not be overlooked that water does not dissolve carbon dioxide instantly—but that time and the surface exposed are important considerations. In dispensing chimney gas to classes from the sampling apparatus—Fig. 355—under a pressure of 4 to 6 ft. of water, the writer has repeatedly observed the fact that the last sample would often show more carbon dioxide than the first, even after 15 minutes standing. The converse of the proposition seems to hold true, as the writer has heated samples of water 10° above the saturation point for 24 to 48 hours without the water giving up the excess oxygen.[4, 5]

The foregoing procedure applies to sampling gases from a boiler or flue. To sample city gas, it should be allowed to burn until the old gas is certainly out of the piping, or it can be blown out into the outside air.

MEASUREMENT AND EXAMINATION OF GASES

Gases are analyzed in two ways—by absorption of a certain constituent, and noting the diminution either in the gas volume or the strength of the reagent used; and by combustion, where the constituents do not lend themselves to absorption. The absorption of oxygen from the air by potassium pyrogallate is an example of the first method and the combustion of methane and subsequent absorption of the carbon dioxide, of the second.

The diminution in volume implies some method of measurement of gas volumes, which brings us to the consideration of meters.

For the measurement of gas in large quantities meters are used. Several types of instrument are available for this purpose.

	Measurement	Permissible Velocity, Feet per Second	Limit of Accuracy,[6] %
Wet meter	Volume	(100 r.p.m.)	0.5
Dry meter—diaphragm type	"	—	±2.0
Dry meter—Connersville type	"	1.6–71	—[7]
Pitot tube	Velocity	Above 8	1
Rotameter or Thorp gauge	"		
Thomas electric	Weight	3 to 500	0.5
Orifice	Velocity	Unlimited	2.0
Venturi tube	"	"	1.0
Anemometer	"	1 to 40	1–5

Of all these instruments, the wet meter and Thomas meter are probably the most accurate. They, however, like some of the others, cannot be used with corrosive gases, being constructed of metal; hence the Pitot tube and rotameter are the ones to be employed in chemical works.

[4] Technology Quarterly, **5**, 250 (1892).
[5] See also Ind. Eng. Chem., Anal. Ed., **7**, 37 (1935).
[6] Taken partly from Marks' "Mechanical Engineers' Handbook."
[7] Said to be accurate.

The *wet meter* consists of a cylindrical drum divided into four spiral compartments, suspended in a bath of water, surrounded by a tight casing: the pressure of the gas causes the drum to rotate, emptying a drumful of gas into the casing and pipes. It must be set level, the water level carefully adjusted to the mark on the glass gauge, with its top open, as well as the inlet and outlet pipes of the meter. The higher the water level the faster the meter. The *dry meter* consists of a pair of metal bellows, with sides of leather soaked in oil, on either side of a diaphragm, and connected with slide valves so that a bellowsful of gas is alternately emptied into the upper part of the meter and piping. The vibrations of the bellows produced by the gas pressure are transmitted to clockwork and indexes. It is to be noted that the indexes apparently read one-tenth of the actual volume passed: the index must make a complete circuit to register the amount stamped on the dial. A small index and dial are usually present for testing the meter, and a tolerance of 2% is allowed by law. This testing is done by meter-provers, carefully calibrated gas holders kept at constant temperature and the rate determined at different speeds. The meter-provers are, in their turn, calibrated by a cubic foot, standardized at the Bureau of Standards. It should be noted that all this calibration is corrected, not to standard conditions (0° C. and 760 mm.), but to the cubic foot as fixed by law—gas saturated with moisture at 60° F. and 30 inches.[8]

The **Connersville meter** is the pump of that name, or Roots blower, in which the flow of gas operates the two figure 8 vanes connected with an index.

The Pitot Tube.—Fig. 356. This consists of two glass tubes, *D*, of about ¼ to 1 inch internal diameter, inserted in the gas stream: one is bent at right angles and is set so that it receives the impact of the gas movement; the other merely registers the pressure of the gas in the pipe. The impact tube should have a straight portion parallel to the air flow, of a length about 10 times the internal diameter of the tube. The open end should be fire polished.[9] The point of insertion of these tubes in the chimney or duct should be in a long straight run of pipe, so as to be as free from eddies as possible. The tube when inserted should be preceded by 10 to 20 diameters of straight duct or pipe and followed by about 5 diameters.[9] Davis[10] says that authorities differ as to whether the tubes should be a third or one-sixth of the diameter from the circumference to show the mean speed: he states further that each flue or chimney is a separate problem and as a result of hundreds of measurements there seems to be "no settled proportionate distance corresponding to the mean velocity."

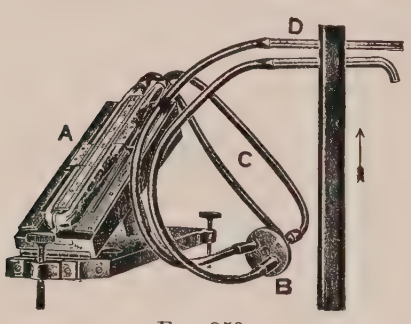

Fig. 356.

The glass tubes are connected by rubber tubing, *C*, through a reverser, *B*, with a U-tube *A*, which is either set vertically, inclined 30°, or one in ten—this

[8] 2° F. makes a difference of about 0.5% in the volume.

[9] Marks' Handbook.

[10] "Handbook of Chemical Engineering," 1, 197; also for the tables for its use. Also Walker, Lewis and McAdams "Principles of Chemical Engineering" or Marks' Handbook.

carries a vernier reading to hundredths of an inch so that readings to thousandths are feasible. The U-tube is filled with solutions of different specific gravity, although ether of 0.74 sp.gr. is the one commonly employed. The difference between the arms of the U-tube represents the difference between the kinetic and static pressures of the gas in the flue or chimney.

The formula for calculating the velocity recommended by W. W. Scott is

$$V = 1290 \sqrt{\frac{\frac{1}{2}h(1+.002176t)}{BM}},$$

where h = vertical differential of gauge reading in terms of inches of water. $\frac{1}{2}$ the reading is taken as the actual reading is double that due to flow pressure alone. B = barometric pressure of the gas in inches of mercury (29.92″). M = specific gravity compared with $H = 1$. Air = 14.39. t = temperature of the gas. V = velocity in feet per second. The formula $V = 42\sqrt{h}$ gives fairly accurate results. Davis' formula is

$$V_0 = \sqrt{\frac{h459+t^0}{519}} \times 28.55.$$

Marks says of the Pitot tubes that they "are the most satisfactory devices for the measurement of gas in large volumes."

The Rotameter, Fig. 357.—This is a German instrument depending upon the height to which a float is carried in a glass tube by the velocity of the stream of gas. A modification of it was used by some of the gas-lighting companies under the name of the Thorp Gauge.

It consists of a graduated glass tube fixed upon a tripod and provided with a plumb line so that it can be set vertically: gas passes in at the lower end, raises the clay or talc float to a certain height and passes out at the top. The height to which the float is raised is noted on the graduations of the tube. The formula for its use is

$$V_1 = V \sqrt{\frac{M}{M'}}.$$

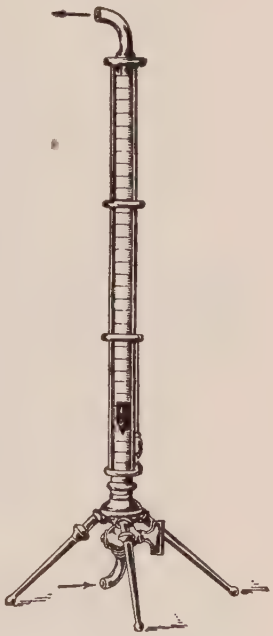

Fig. 357.

V = volume gas as shown by reading of instrument, M its specific gravity = 1.0.

V = volume desired, M_1 = sp.gr. of gas.

It is made in all capacities from 0.2 cu. ft., per hour up.

The Thomas Electric Gas Meter.—This depends upon the principle that if the specific heat of the gas be known, and an amount of energy be put into it, by means of a coil, sufficient to keep a certain difference of temperature between two thermometers, one before and one after the coil, this energy is a direct measure of the volume of gas flowing. Two electrical thermometers are placed in the stream of gas with a heating coil between them: 2° difference of tempera-

ture is automatically maintained between the thermometers and the energy to preserve this difference of temperature (.0127 watt hour per standard unit of gas) is read off on the meter as cubic feet of gas. It is independent of temperature or pressure changes in the gas, and is used up to gas pressures of 180 lbs. per square inch. This is used in a Western gas works measuring 200,000 ft. of gas per hour.

The Orifice Meter.[11]—In this the same principle is used as in measuring water, by determining the diminution in pressure as registered on delicate gauges before and after the gas has passed through a standard orifice. It is largely used for measuring natural gas, the entrained sand in which enlarges the orifice.

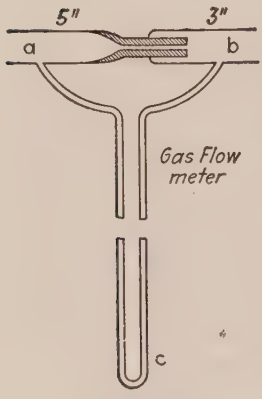

Fig. 358.

The Anemometer is used ordinarily for measuring currents of air leaving or entering a room, analogous to its employment in meteorology.

The Gas Flow Meter.[12]—This consists of a tube *a*, into which capillaries *b* of different sizes can be inserted by a rubber stopper (one at a time). On either side of the capillary is a T, the stems of which are joined together, making a U-gauge *c*. This, when filled with water shows the difference in pressure of the gas before and after passing through the capillaries. The apparatus is calibrated by a wet or dry meter. It has a capacity of from 0.5 to 500 liters (0.0176 to 17.6 cu. ft.) per hour. See Fig. 358.

The Venturi Meter.—Fig. 359 is an apparatus consisting of a steeply conical tube connected to one less steep, producing a constriction, which is inserted in the pipe line conveying the gas. From the pressures each side of the constric-

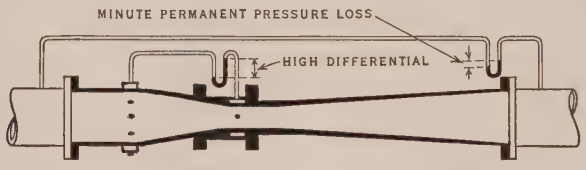

Fig. 359.

tion and its size the quantity of gas passing can be determined. For its use see Marks' " Handbook " or Walker, Lewis and McAdams, " Principles of Chemical Engineering."

Measurement of Gas in Small Quantities. Gas Burettes

Here may be mentioned the Hempel gas burette, made for accurate work with a compensation tube; the bulbed Orsat or Bunte burette; the separatory

[11] See in this connection, "Measurement of Gas and Liquids by Orifice Meter," Westcott and Diehl, Metric Metal Works, Erie, Pa. Publishers. Also Bureau of Standards, Circular No. 309 (1926), "Gas Measuring Instruments."

[12] Benton, Ind. Eng. Chem., **11**, 623 (1919). Also article by Dodge, "Measurement of Gases and Vapors," Ind. Eng. Chem., **24**, 361 (1932).

funnel and graduate. Fuwa and Shattuck [13] measure quantities of 30–200 ml. per minute by bubbling through water or dilute sulfuric acid.

The Hempel Gas Burette, Fig. 366, consists of a 100-ml. burette graduated in fifths of a cubic centimeter, provided with a short capillary at the top and closed with a rubber connector and pinchcock, and a wider tube at the bottom, over which a 3/16-in. rubber tube is drawn, which connects it with the leveling tube of similar size and length to the burette. It is manipulated by filling the leveling tube completely with water, opening the pinchcock on the top of the burette and filling it with water. The gas to be analyzed is sucked in and measured as with the Orsat apparatus, Fig. 364. Both burettes must be calibrated as is customary in volumetric analysis, and the water saturated with the gas to be analyzed. The water may be acidified and a few drops of an indicator added to turn it pink; this shows if any alkali accidentally runs over into the burette.

Separatory Funnel and Graduate, Fig. 372.—From the water which has flowed out, the quantity of gas can be determined.

Standards of Measurement.—The unit volume of gas for scientific purposes is measured dry at 0° C. and 760 mm. pressure: the legal or industrial cubic foot in English speaking countries is measured saturated with water vapor, at 60° F. and 30 inches barometric pressure. The gas is therefore actually under a pressure equal to the height of the barometer diminished by the tension of aqueous vapor (in inches) at the temperature at which the gas is confined: this is given in Table 2 of the Appendix.

In ordinary gas analysis, it is unusual to correct a gas volume, as barometric changes during the analysis are negligible, and the laboratory temperature is commonly kept very constant. In case corrections are necessary, we correct first for *pressure* (Law of Boyle, $V : V' : : P' : P$): the height of the barometer is read, its temperature taken, and its height in millimeters reduced to 0° C. $= B$. The tension of aqueous vapor at the temperature at which the volume of the gas is read is determined from tables, Table 2,—Aq and is deducted from the barometric height: in case the gas be under pressure M, as of a pipe line, this is changed to millimeters of mercury, and added to these figures. The formula is $V_0 = V_{(obs.)} \times \frac{B - Aq + M}{760}$, V_0 being the corrected and $V_{(obs.)}$ the observed volume.

Correcting next for *temperature* (Law of Charles $V : V' : : T : T'$) the formula is $V_0 : V_{(obs.)} : : T_0 : T_{(obs.)}$, T being in absolute degrees

$$V_0 = V_{(obs.)} \times \frac{273}{273 + T° \text{ C.}} = \frac{1}{1 + 0.00367\ T° \text{ C.}};$$

then the formula becomes $V_0 = V_{(obs.)} \times \frac{1}{1 + 0.00367\ T° \text{ C.}}$.

Tables giving factors for $1 + 0.00367\ T°$ C. for a wide range of temperature are to be found in the ordinary " Handbooks of Chemistry and Physics."

[13] Ind. Eng. Chem., **15**, 230 (1923). See also Page, "Constant Flow Orifice Meters," Ind. Eng. Chem., Anal. Ed. **7**, 355 (1935).

For reduction to conditions prevailing in the gas industry, "Industrial Standard Conditions," i.e., 30 inches, saturated with water, at 60° F., the formula is

$$V_0 = V_{(obs.)} \times \frac{B - Aq + M}{30'' - 0.51''} \times \frac{520° \text{ F.}}{460 + T° \text{ F.}}.$$

B, Aq and M are in inches of mercury: 0.51 inch is the tension of aqueous vapor at 60° F. In practice this reduction is obtained from Table 9 (Appendix).

Specific Gravity.—The specific gravity of a gas is usually referred to air as unity: it can be readily calculated by dividing the molecular weight of the gas by 28.95, the weight in grams of 22.4 liters of air (22.4 liters will be remembered as the gram-molecular volume).

Specific gravity can be directly determined by Jenkins' apparatus, p. 2397, or the Edwards gas balance.[14, 15]

This depends upon an indirect weighing of the gases. The apparatus consists of a closed vessel counterpoised in a water-jacketed cylinder of the gas; this is connected with a mercury gauge. Dry air is passed into the cylinder and pressure applied to it until the vessel just balances at a predetermined point and the gauge reading noted. The operation is repeated with the gas to be tested. The densities of the gases must be the same at these pressures; or the densities of the two gases at normal pressure are in the inverse ratio of the pressures, when of equal buoyant force. Results accurate to 0.2% are obtained and no calibration is required. It has given trouble at times owing apparently to leaks in the "closed vessel" mentioned.

With the effusion method results are dependent upon the orifice used, the pressure and the confining medium. They may vary as much as 10% with different observers. The orifice should be 0.18–0.3 mm. in diameter in a plate 0.04 mm. or less thick: the pressure should not be allowed to fall below 2 inches of water: results to an accuracy of 2% may be expected.

Absorption Apparatus, Tubes and Pipettes

These are quite varied according to the purpose for which they are intended. A very efficient form is the Friedrichs Spiral Gas Washing bottle, Fig. 360; here the gas has to pass through a long spiral path. Dennis recommends this for the absorption of sulfur dioxide. The gas is run through a solution until a color change takes place. Were the reagent to be washed out and titrated it would not seem so well adapted on account of the difficulty of thoroughly washing it.

The Varrentrapp and Will bulbs, Fig. 361, the use of which is evident from the figure, are used for the absorption of ammonia in illuminating gas. The Wolff absorption tube, Fig. 362, the empty arm of which is filled with beads or broken glass, is used for the absorption of carbon monoxide by blood. The bulbed tube, provided with a small jet, is generally used for containing standard solutions of acid, alkali, or potassium permanganate or, in general, a solution which is to be titrated after absorption. Where the presence of a gas as, for example, water vapor is to be determined by the increase of weight of the reagent used, Winkler's spiral, Fig. 363,[16] may be employed.

[14] Ind. Eng. Chem., **9**, 790 (1917). Bur. Stds. Techn. Bull. No. 94.
[15] Improvements by Warren, C. A., **30**, 2425.

Fig. 360.

Fig. 361.

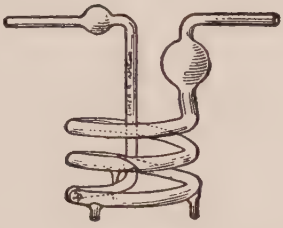

Fig. 363.

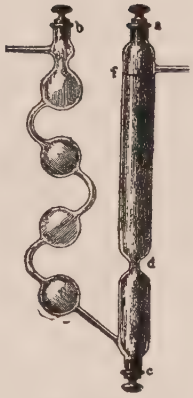

Fig. 362.

Pipettes.—Particularly for the Orsat Apparatus, Fig. 364. These are ordinarily filled with glass tubes, but various modifications have been proposed: these are the bubbling type of Hankus, the spiral bubbling variety of Nowicki-Heinz and a combination of the Friedrichs wash bottle proposed by Dennis. All these suffer from the very serious disadvantage of a glass three-way stopcock at the top, which it is practically impossible to prevent from sticking, unless the apparatus be used by one person and that one exceptionally careful and painstaking. Dennis has shown that one variety is no more rapid than the original and some of the others but little more so. When it is further considered that they cost four times as much, their use would seem of doubtful expediency.

It is interesting to note further that Anderson [17] has shown that with the modified potassium pyrogallate which he uses, the original Orsat slightly modified, to allow the precipitate to settle, is the best. Francis of the U. S. Steel Corporation laboratory has devised a bubbling pipette with automatic valve, which is very effective: Shepherd of the Bureau of Standards has also devised a bubbling pipette in which the gas is delivered into the reagent through a fine platinum sieve making a quantity of fine bubbles. It would seem likely that the holes in the platinum might become clogged by the standing of the reagent. Both of these are very expensive.

Examination of the Gases

The qualitative examination of a gaseous mixture is rarely resorted to in technical work: a sufficiently close idea of the gases present can be obtained by a consideration of the reactions involved in the various operations. It is, however, not safe to rely upon this in matters of importance, as conditions may change: for example if the gases be dry or dilute, hydrogen sulfide and sulfurous anhydride can exist together. Similarly in sewage gases, the gas absorbed by cuprous chloride is probably not wholly carbon monoxide but higher paraffin hydrocarbons. The means of identifying the different gases will be found under each gas.

[16] Called "Winkler's Bulbs" in the apparatus catalogs.

[17] Ind. Eng. Chem., **8**, 131–3 (1916).

Gases are sometimes tested by burning them and investigating the products of combustion. Often the gas refuses to burn, as in the case of wood gas, as it contains so much incombustible gas (30% CO_2): this is removed with caustic alkali and the burning test repeated. In performing this test, particularly with electrolytic gases, it must be remembered that they may contain enough oxygen or chlorine to support their own combustion like "detonating gas." A glass tube 18 inches long well packed with glass beads, broken glass or porcelain must always be inserted between the gas holder and the jet: this will extinguish the flame of the gas wave, should it start, after the manner of the gauze in the Davy safety lamp, and prevent flame from reaching the explosive mixture in the gas holder with serious results. Sufficient pressure should of course be maintained on the holder itself.

Detection and Determination of the Various Gases

Clemens Winkler [18] divided the gases into seven groups according to their behavior with various solvents. These were contained in suitable absorption tubes or vessels and the gases passed through them. His scheme was as follows:

Gases absorbed by

I. H_2SO_4 1.7 sp.gr.; NH_3, (N_2O_3), N_2O_4.[19]
II. KOH 1.3 sp.gr.; Cl_2, HCl, $(CN)_2$, HCN, SO_2, H_2S, SiF_4, CO_2.
III. $AgNO_3$; PH_3, AsH_3, SbH_3.
IV. Pyrogallol; O_2, (O_3).
V. CuCl; CO.
VI. Acid $FeSO_4$ 1 : 2; NO.
VII. Unabsorbed; H_2, CH_4, C_2H_2, C_2H_4, N_2O, N_2, COS, and the noble gases.

The following tables give the specific gravity referred to air, the solubility in water at 20°, the qualitative tests and quantitative methods of determination of these gases: additional means will be found mentioned under the several gases themselves.

Group I

Gases Absorbed by H_2SO_4 1.7 sp.gr.

Name	Ammonia	Nitrous anhydride	Nitrogen tetroxide
Gravity, air = 1	0.5971		1.5906
Qualitative tests	Fumes w. HCl on a rod. Nessler's reagent	Acts like a mixture of NO and NO_2	Absorb in KOH, test for nitrites
Quantitative det'n.	Absorption in standard acid. Or $3NaBrO + 2NH_3 = N_2 + 3NaBr + 3H_2O$. Or absorption in water and Nesslerization		Absorption in N/10 $KMnO_4 \cdot 2KMnO_4 + 10NO_2 + 3H_2SO_4 + 2H_2O = 10HNO_3 + K_2SO_4 + 2MnSO_4$. Or in standard alkali
Solubility 20° C., 1 ml. water absorbs ml.	702		Forms HNO_3, HNO_2

[18] "Die Industrie Gase," 1876–1879.

[19] Sulfuric acid of this strength dissolves appreciable quantities of propane, propene, butane and butene.

Group II

GASES ABSORBED BY KOH 1.3 SP.GR.

Name	Chlorine	Hydrochloric acid	Cyanogen
Gravity, air = 1	2.4494	1.268	1.7968
Qualitative test	KI starch paper	Fumes w. NH_3	Pass through mixture of $FeSO_4$ 1 : 10 + KOH 1 : 3, and ppt. as Prussian blue w. ferric alum and H_2SO_4 [20]
Quantitative det'n.	$2KI+Cl_2=2KCl+I_2$. Or absorption w. KOH	Absorption in standard alkali or silver nitrate	
Solubility 20° C., 1 ml. water absorbs ml.	2.29	444	4.5

Hydrocyanic acid	Sulfur dioxide	Hydrogen sulfide	Silicon fluoride	Carbon dioxide
0.9359	2.224	1.1769	3.60	1.5290
Absorption in KOH and $FeSO_4$ and $FeCl_2$ = Prussian blue. Absorption w. KOH or acid $AgNO_3$ [21]	Fuchsine paper bleached or KIO_3 starch paper. $SO_2+2I+2H_2O=H_2SO_4+2HI$	$PbAc_2$ paper, absorption by I solution. $H_2S+2I=2HI+S$	None. $3SiF_4+4H_2O=SiO_4H_4+2H_2SiF_6$	BaO_2H_2 on black rod. Absorption w. KOH or BaO_2H_2 and titration
Very sol.	39.3	2.90	Decomposed	0.874

Group III

GASES ABSORBED BY $AgNO_3$

Name	Hydrogen phosphide, phosphine	Hydrogen arsenide, arsine	Hydrogen antimonide, stibine
Gravity, air = 1	1.1829	2.695	4.360
Qualitative test	Neutral H_2O solution $KI+HgI_2$ = cryst. orange yel. ppt. PHg_3I_3 [22]	Blk. ppt. of $AsAg_3$ w. $AgNO_3$	Blk. ppt. of $SbAg_3$ w. $AgNO_3$
Quantitative det'n.	Pass through Br water and ppt. H_3PO_4 as usual	Absorb w. NaClO cont. 3% Cl [23]	Decompose w. tartaric acid and det. Sb
Solubility 20° C., 1 ml. water absorbs ml.	0.02	About 5	Slight

[20] Nauss, J. Gasbeleuchtung, **43**, 969 (1900).
[21] Rhodes, J. Ind. Eng. Chem., **4**, 652 (1912).
[22] Lemoult, Compt. rend., **139**, 478 (1904).
[23] Reckleben, Z. angew. Chem., **19**, 275 (1906).

	Group IV		Group V	Group VI
	Absorbed by potassium pyrogallate		Absorbed by cuprous chloride	Absorbed by $FeSO_4$ 1 : 2 acidulated w. H_2SO_4
Name	Oxygen	Ozone	Carbon monoxide	Nitric oxide
Gravity, air = 1	1.1052	1.624	0.9671	1.0367
Qualitative test	Darkening of light brown "pyro"	$MnCl_2$ paper; KI starch paper, N_2O_4 and H_2O_2 being removed by $KMnO_4$	Absorb in blood, and examine w. spectroscope	Oxidize, absorb in KOH and test for nitrites
Quantitative det'n	By "Pyro." CuCl in absence of CO		Absorption w. CuCl	Absorb in $FeSO_4$ 1 : 2 acidulated w. H_2SO_4 or with $KMnO_4$ as N_2O_4
Solubility 20° C., 1 ml. water absorbs ml.	0.0317	0.6 at 0°	0.0231	0.470

Group VII

UNABSORBED

Name	Hydrogen	Methane	Ethylene (ethene)	Acetylene (ethine)
Gravity, air = 1	0.0694	0.5545	0.9684	0.9056
Qualitative test	Dry $PdCl_2$ gives HCl	None		Red ppt. w. am. CuCl (explosive!)
Quantitative det'n	By combustion or explosion w. O_2	By combustion or explosion w. O_2	Absorption w. Br water or $H_2S_2O_7$	As C_2H_4, which see
Solubility 20° C., 1 ml. water absorbs ml.	0.0183	0.0330	0.122	1.03

Nitrous oxide	Carbon oxysulfide	Nitrogen	The noble gases
1.5301	2.075	0.9673	Helium, Neon, Argon, Krypton, Xenon
None	None	None	
By explosion with H_2 or combustion w. CuO	Alcoholic KOH 1 : 3 in 66% alchol by weight	By absorption or combustion of all other gases and measuring the residue which also contains the noble gases	
0.670	0.568	.0159	

NOTES.—Group I: NaBrO is made by saturating a 10% solution of caustic soda with bromine.

Group II: Chlorine can be removed from hydrochloric acid by passing the gases over finely powdered antimony: hydrochloric acid can be removed from chlorine by means of manganese dioxide or zinc oxide.

Cyanogen is not absorbed by acid silver nitrate solution, from which it can be separated by drawing air through it: hydrocyanic acid is precipitated under these conditions.

ANALYSIS OF GASES

The analysis of a gaseous mixture is effected by absorbing the various constituents and observing the diminution in volume: in case the gas be unabsorbable, as for example methane (CH_4), it is burned and the carbon dioxide and water determined.

(a) **Analysis of mixtures for carbon dioxide, oxygen and carbon monoxide (e.g., chimney gases, producer and blast furnace gas)** can be done with any of the apparatus to be described. The Orsat, or Elliott are the forms usually employed.

(b) **Analysis of mixtures as in (a) and also containing combustible gases as hydrogen and methane,** e.g., city gas.

The Orsat Apparatus. Description.—The apparatus,[24] Fig. 364, is enclosed in a case to permit of transportation from place to place; furthermore, the measuring tube is jacketed with water to prevent changes of temperature affecting the gas volume. The apparatus consists essentially of the leveling bottle *A*, the burette *B*, the pipettes *P'*, *P''*, *P'''*, and the connecting tube *T*. Pipette *P'* is filled with potassium (or sodium) hydroxide solution (see Reagents) so that when it is drawn up into the front arm about half an inch in depth is left in the rear arm. Pipettes *P''* and *P'''* are similarly filled with potassium (or sodium) pyrogallate and cuprous chloride solutions respectively. These reagents require to be protected from the oxygen of the air by collapsible rubber bags of good quality. As the oxygen in the air over the reagent is absorbed, a diminution in pressure takes place rendering it difficult to bring the reagent to the point on the stem: the obvious remedy is to remove the bag temporarily and adjust the reagent. When the apparatus is first set up, one or two blank analyses should be made, to saturate the water and reagents with the gases. For example the potassium hydroxide absorbs carbon dioxide, it also absorbs about 3 ml. of oxygen, 2 ml. of carbon monoxide and 1.5 ml. of nitrogen, by virtue of the 100 ml. of water which it contains. A change of temperature of 1° makes a change of 0.36 of the volume of the gas: a change of pressure of 1 mm. produces 0.13 change in the volume.

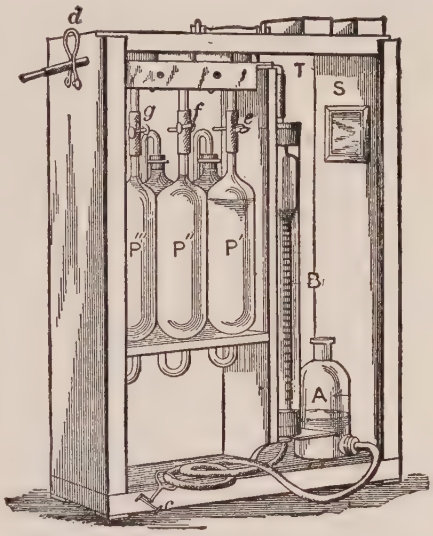

Fig. 364.

Manipulation.—The reagents in the pipettes should be adjusted in the capillary tubes to a point on the stem about midway between the top of the pipette

[24] The apparatus shown is one of the simplest and least expensive forms: it has proved itself well adapted for occasional use. Hayes has constructed it in a very attractive and compact form in metal.

and the rubber connector. This is effected by opening wide the pinchcock upon the connector, the bottle being on the table, and very gradually lowering the bottle until the reagent is brought to the point above indicated. Six inches of the tubing used correspond to but 0.1 ml., so that an error of half an inch in adjustment of the reagent is without influence upon the accuracy of the result. The reagents having been thus adjusted, the burette and connecting tube are completely filled with water by opening *d* and raising the leveling bottle. The apparatus is now ready to receive a sample of gas (or air for practice). In case a flue-gas is to be analyzed *d* is connected with *i*, Fig. 354, *A* lowered and about 102 ml. of the gas forced over by opening *h*; or *d* may be connected with a T-joint in the gas stream; the burette after filling is allowed to drain one minute by the sand glass, *c* snapped upon its rubber tube, and the bottle *A* raised to the top of the apparatus. By gradually opening *c* the water is allowed to run into the burette until the lower meniscus stands upon the 100 or 0 mark (according to the graduation of the apparatus). The gas taken is thus compressed into the space occupied by 100 ml. and by opening *d* the excess escapes. Open *c* and *bring the level of the water in the bottle to the same level as the water in the burette* and take the reading, which should be 100 ml. Special attention is called to this method of reading: if the bottle be raised, the gas is compressed; if lowered, it is expanded.

Determination of Carbon Dioxide.—The gas to be analyzed is invariably passed first into pipette *P'*, containing potassium hydroxide for the absorption of carbon dioxide, by opening *e* and raising *A*. The gas displaces the reagent in the front part of the pipette, laying bare the tubes contained in it, which being covered with the reagent present a large absorptive surface to the gas; the reagent moves into the rear arm of the pipette, displacing the air over it into the flexible rubber bag which prevents its diffusion into the air. The gas is forced in and out of the pipette by raising and lowering *A*, the reagent finally brought approximately to its initial point on the stem of the pipette, the burette allowed to drain one minute and the reading taken. The difference between this and the initial reading represents the milliliters of carbon dioxide present in the gas. To be certain that all the carbon dioxide is removed, the gas should be passed a second time into *P'* and the reading taken as before; these readings should agree within 0.1%, and are called " check readings."

Determination of Oxygen.—The residue from the absorption of carbon dioxide is passed into the second pipette, *P''*, containing an alkaline solution of potassium pyrogallate, until no further absorption will take place. The difference between the reading obtained and that after the absorption of carbon dioxide, represents the number of milliliters of oxygen present.

Determination of Carbon Monoxide.—The residue from the absorption of oxygen is passed into the third pipette, *P'''*, containing cuprous chloride, until no further absorption takes place; that is, in this case until readings agreeing exactly (not merely to 0.1) are obtained. The difference between the reading thus obtained and that after the absorption of oxygen, represents the number of milliliters of carbon monoxide present.

Determination of Hydrocarbons.—The residue left after all absorptions have been made may consist, in additon to nitrogen, the principal constituent, of hydrocarbons and hydrogen: see p. 2356.

Accuracy.—The apparatus gives results accurate to 0.2 of 1%, hence figures obtained by division to 0.01 should not be reported.

Time Required.—About twenty minutes are required for an analysis; two may be made in twenty-five minutes, using two apparatus.

NOTES.—The method of adjusting the reagents is the only one which has been found satisfactory: if the bottle be placed at a lower level and an attempt made to shut the pinchcock *c* upon the connector at the proper time, it will almost invariably result in failure.

The process of obtaining 100 ml. of gas is exactly analogous to filling a measure heaping full of grain and striking off the excess with a straight edge; it saves arithmetical work, as milliliters read off represent per cent directly.

It often happens when *e* is opened, *c* being closed, that the reagent *P'* drops, due not to a leak, as is usually supposed, but to the weight of the column of the reagent expanding the gas.

The object of the rubber bags is to prevent the access of air to the reagents, those in *P''* and *P'''* absorbing oxygen with great avidity, and hence if freely exposed to the air would soon become useless. These bags if well made will last two years and amply protect the solution: or a "sealing pipette" can be used for the pyro.

Carbon dioxide is always the first gas to be removed from a gaseous mixture. In the case of air the percentage present is so *small*, 0.08 to 0.1, as scarcely to be seen with this apparatus. It is important to use the reagents in the order given; if by mistake the gas be passed into the second pipette, it will absorb not only oxygen, for which it is intended, but also carbon dioxide; similarly if the gas be passed into the third pipette, it will absorb not only carbonic oxide, but also oxygen as well.

The use of pinchcocks and rubber tubes, original with the author, although recommended by Naef, is considered by Fischer to be inaccurate. The experience of the author, however, does not support this assertion, as they have been found to be fully as accurate as glass stopcocks, and very much less troublesome and expensive.

In case any potassium hydroxide or pyrogallate be sucked over into the tube *T* or water in *A*, the analysis is not spoiled, but may be proceeded with by connecting on water at *d*, opening this cock, and allowing the water to wash the tubes out thoroughly. The addition of a little hydrochloric acid to the water in the bottle *A* will neutralize the hydroxide or pyrogallate, and the washing may be postponed until convenient: Methyl orange indicator may be added to be sure the water is acid.

After each analysis the number of milliliters of oxygen and carbonic oxide should be set down upon the ground-glass slip provided for the purpose. By adding these numbers and subtracting their sum from the absorption capacity (see Reagents) of each reagent, the condition of the apparatus is known at any time, and the reagent can be renewed in season to prevent incorrect analyses.

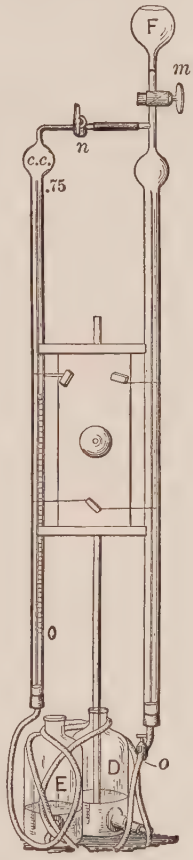

FIG. 365.

Elliott Apparatus. Description.—The apparatus,[25] Fig. 365, consists of a burette holding 100 ml. graduated in tenths of a milliliter and bulbed like the Bunte apparatus—the bulb holding about 30 ml.; it is connected with a leveling bottle similar to the Orsat apparatus. The top of the burette ends in a capillary stopcock, the stem of which is ground square to admit of close connection with the "labora-

[25] The simplest form is here shown as being best adapted for teaching purposes.

tory vessel," an ungraduated tube similar to the burette, except of 125 ml. capacity. The top of this " vessel " is also closed with a capillary stopcock, carrying by a ground-glass joint, or better a rubber stopper, a thistle-tube *F*, for the introduction of the reagents. The lower end of this " vessel " is closed by a rubber stopper carrying a three-way cock *o*, and connected with a leveling bottle *D*. The burette and vessel are held upon a block of wood—supported by a ring stand—by fine copper wire tightened by violin keys.

Manipulation.—The ground-glass joints are lubricated with stopcock grease. The leveling bottles are filled with water, the stopcocks opened, and the bottles raised until the water flows through the stopcocks *m* and *n*. *m* is connected with the source whence the gas to be analyzed is to be taken, *n* is closed, *D* lowered and rather more than 100 ml. drawn in, and *m* closed. *n* is opened, *D* raised and *E* lowered, nearly 100 ml. of gas introduced, and *n* closed; by opening *m* and raising *D* the remainder of the gas is allowed to escape, the tubes being filled with water and *m* closed. *n* is opened and the water brought to the reference mark; the burette is allowed to drain one minute, the level of the water in *E* is brought to the same level as in the burette, and the reading taken.

Determination of Carbon Dioxide.—By raising *E*, opening *n*, and lowering *D*, the gas is passed over into the laboratory vessel; *F* is filled within half an inch of the top with potassium hydroxide, *o* closed, *m* opened, and the reagent allowed slowly to trickle in. A No. 3 evaporating dish is placed under *o*, and this turned to allow the liquid in the laboratory vessel to run into the dish. At first this is mainly water, and may be thrown away; later it becomes diluted reagent and may be returned to the thistle-tube. When the depth of the reagent in the thistle-tube has lowered to half an inch, it should be refilled either with fresh or the diluted reagent and allowed to run in until the absorption is judged to be complete, and the gas passed back into the burette for measurement. To this end close *o* and then *m*, raise *E*, open *n*, and force some pure water into the laboratory vessel, thus rinsing out the capillary tube. Now raise *D* and lower *E*, shutting *n* when the liquid has arrived at the reference mark. The burette is allowed to drain a minute, the level of the water in the bottle *E* brought to the same level as the water in the burette, and the reading taken.

Determination of Oxygen.—The manipulation is the same as in the preceding determination, potassium pyrogallate being substituted for potassium hydroxide; the apparatus requiring no washing out.

Determination of Carbon Monoxide.—The laboratory vessel, thistle-tube, and bottle if necessary, are washed free from potassium pyrogallate and the absorption made with acid cuprous chloride similarly to the determination of carbon dioxide. The white precipitate of cuprous chloride may be dissolved by hydrochloric acid.

Accuracy and Time Required.—The apparatus is as accurate for absorptions as that of Orsat; it is stated to be much more rapid—a claim which the writer cannot substantiate. It is not as portable, is more fragile, and more troublesome to manipulate, and as the burette is not jacketed, it is liable to be affected by changes of temperature.

NOTES.—In case at any time it is desired to stop the influx of reagent, *o* should be closed first and then *m*; the reason being that the absorption may be so rapid as to suck air in through *o*, *m* being closed.

The stopcock should be so adjusted as to cause the reagent to spread itself as completely as possible over the sides of the burette.

By the addition of an explosion tube it is used for the analysis of city gas,[26] bromine being used to absorb the "illuminants," Winkler [27] states that this absorption is incomplete; later work by Treadwell and Stokes, and also Korbuly,[28] has shown that bromine water, by a purely physical solution, does absorb the "illuminants" completely; Hempel [29] states that explosions of hydrocarbons made over water are inaccurate, so that the apparatus can be depended upon to give results upon methane and hydrogen only within about 2%. It is, however, very rapid, a complete analysis of city gas can be made with it in fifty-five minutes.

Hempel's Apparatus. Description.—The apparatus,[30] Figs. 366 and 367, is very similar in principle to that of Orsat; the burette is longer, admitting of

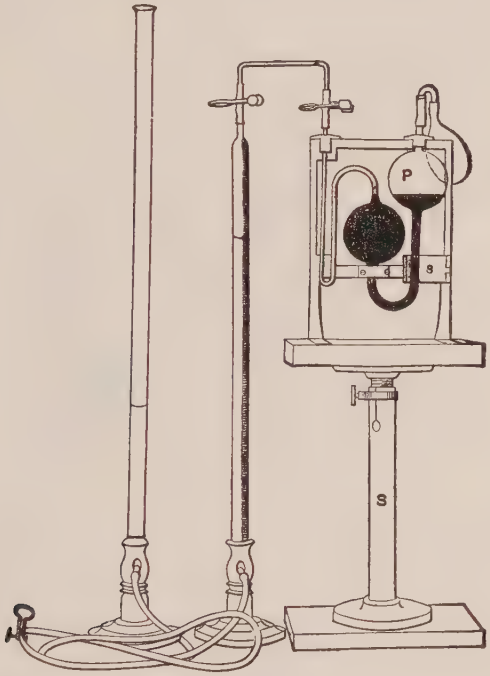

Fig. 366.

the reading of small quantities of gas and the pipettes are separate and mounted in brass clamps on iron stands. *P* shows a " simple " pipette [31] provided with a rubber bag; this form, after forty years of use, can be said satisfactorily to take the place of the cumbersome " compound " pipette.

[26] Mackintosh, Am. Chem. Jour., **9**, 294 (1887).
[27] Zeit. Anal. Chem., **28**, 286 (1889).
[28] Treadwell-Hall's "Quantitative Analysis" p. 569.
[29] "Gasanalytische Methoden" p. 102.
[30] The simplest forms are here shown.
[31] Gill, Am. Chem. J., **14**, 231 (1892).

The pipette for fuming sulfuric acid [32] is shown at *F*, and differs from the ordinary in that vertical tubes after the manner of those in the Orsat pipettes replace the usual glass beads. This prevents the trapping of any gas by the filling, which was so common with the beads and glass wool. *E* represents the large explosion pipette,[33] of about 250-ml. capacity, with walls half an inch thick; the explosion wires enter at the top and bottom to prevent short-circuiting; mercury is the confining liquid. The small explosion pipette holds about 110 ml. and is of glass, the same thickness as the simple pipettes. Water is here used as the confining liquid, and acidulated with HCl usually in the burette.

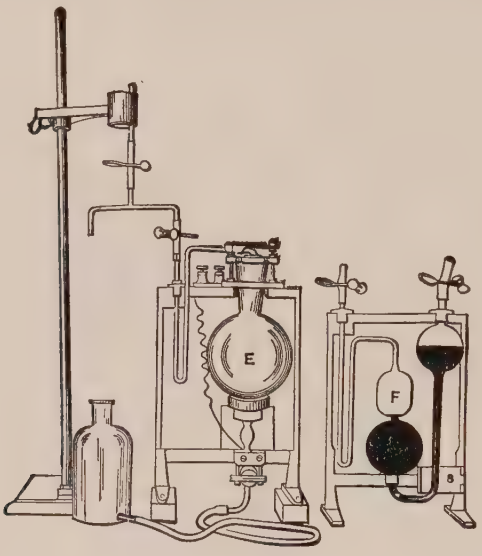

FIG. 367.

A " Ford " induction coil capable of giving a fourth-inch spark, with three dry cells, four " simple " pipettes and a mercury filled burette, complete the outfit.

The burette should be carefully calibrated and the corrections may very well be etched upon it opposite the 10-ml. divisions.

In working with the apparatus the pipettes are placed upon the adjustable stand *S* and connection made with the doubly bent capillary tube.

Manipulation.—To acquire facility with the use of the apparatus before proceeding to the analysis of city gas, it is well to make the following determinations, obtaining " check-readings " in every case: I. Oxygen in air, by (1) absorption with phosphorus; (2) absorption with potassium (or sodium) pyrogallate; [34] (3) by explosion with hydrogen.

[32] Ibid., J. Am. Chem. Soc., **18**, 67 (1896).

[33] Gill, J. Am. Chem. Soc., **17**, 771 (1895).

[34] The writer finds after an experience of more than thirty-five years in the laboratory with hundreds of students, that sodium pyrogallate can be used with practically the same results as the potassium compound. The absorption is complete, as shown by subsequent treatment with cuprous chloride.

I. Determination of Oxygen in Air

(1) **By Phosphorus.**—100 ml. of air are measured out as with the Orsat apparatus, the burette being allowed to drain two minutes. The rubber connectors upon the burette and pipette are filled with water, the capillary tube inserted, as far as it will go, by a twisting motion, into the connector upon the burette, thus filling the capillary with water; the free end of the capillary is inserted into the pipette connector, the latter pinched so as to form a channel for the water contained in it to escape, and the capillary twisted and forced down to the pinchcock. There should be as little free space as possible between the capillaries and the pinchcock. Before using a pipette, its connector (and rubber bag) should be carefully examined for leaks, especially in the former, and if any found the faulty piece replaced.

The pinchcocks on the burette and pipette are now opened, the air forced over into the phosphorus, and the pinchcock on the pipette closed; action immediately ensues, shown by the white fumes; after allowing it to stand fifteen minutes the residue is drawn back into the burette, the latter allowed to drain and the reading taken. The absorption goes on best at 20° C., not at all below 15° C.; it is very much retarded by small amounts of ethane and ammonia. It cannot be used to absorb commercial oxygen. No cognizance need be taken of the fog of oxides of phosphorus.

(2) **By Potassium Pyrogallate.**—100 ml. of air [35] are measured out as before, the carbon dioxide absorbed with potassium hydroxide and the oxygen with potassium pyrogallate, as with the Orsat apparatus; before setting aside the pyrogallate pipette, the number of milliliters of oxygen absorbed should be noted upon the slate *s* on the stand. This must never be omitted with any pipette save possibly that for potassium hydroxide, as failure to do this may result in the ruin of an important analysis. The reason for the omission in this case is found in the large absorption capacity—four to five liters of carbon dioxide—of the reagent.

(3) **By Explosion with Hydrogen.**—Forty-three ml. of air and 57 ml. of hydrogen are measured out, passed into the small explosion pipette, the capillary of the pipette filled with water, the pinchcocks and glass stopcock all closed, a heavy glass or fine wire gauze screen placed between the pipette and the operator, the spark passed between the spark wires, and the contraction in volume noted. *The screen should never be omitted, as serious accidents may occur thereby.* The oxygen is represented by one-third of the contraction. For very accurate work the sum of the combustible gases should be but one-sixth that of the non-combustible gases; otherwise some nitrogen will burn and high results will be obtained;[36] that is, $(H+O) : (N+H) : : 1 : 6$.

II. Analysis of Manufactured or City Gas

One hundred ml. of gas are measured from the bottle containing the sample into the burette.

Determination of Carbon Dioxide.—The burette is connected with the pipette containing potassium hydroxide and the gas passed into it with shaking until no further diminution in volume takes place.

[35] See Anderson's work, J. Ind. Chem., **7**, 587 (1915).
[36] This is shown in the work of Gill and Hunt, J. Am. Chem. Soc., **17**, 987 (1895).

Illuminants, C_nH_{2n}, C_nH_{2n-6} Series.—The gas is passed into saturated bromine water and thoroughly shaken, the bromine fumes removed, with the potassium (or sodium) hydroxide, like the CO_2, and the treatment with bromine and hydroxide repeated until check readings are obtained. The difference between this last reading and that after the absorption of the carbon dioxide represents the volume of " illuminants " or " heavy hydrocarbons " present.

Or fuming sulfuric acid can be employed instead of bromine water, removing the sulfuric and sulfurous anhydrides by potassium hydroxide as in the case of the bromine fumes. Fuming nitric acid is not recommended, as it is liable to oxidize carbon monoxide.

Oxygen.—This is absorbed, as in the analysis of air, by potassium or sodium pyrogallate.

Carbon Monoxide.—The gas is now passed into ammoniacal cuprous chloride, until the reading is constant to 0.2 ml.; it is then passed into a second pipette, which is fresh, and absorption continued until constant readings are obtained. The second pipette should not have absorbed more than 10 ml. of CO.[37]

Gautier and Clausmann [38] have shown that some carbon monoxide escapes solution in cuprous chloride, so that for very accurate work it may be necessary to pass the gas through a U-tube containing iodic anhydride heated to 70° C.

This is done by interposing this tube between the burette and a simple pipette filled with potassium hydrate. The reaction is $5CO+I_2O_5=5CO_2+2I$. The diminution in volume represents directly the volume of carbonic oxide present.

The volume of air contained in the tube should be corrected for as follows: One end of the tube is plugged tightly and the other end connected with the gas burette partly filled with air. A bath of water at 9° C. is placed around the U-tube and the reading of the air in the gas burette recorded when constant; the bath is now heated to 100° and the burette reading again recorded when constant. The increase in reading represents one-third the volume of the U-tube, $273 : 273+(100-9) : : 3 : 4$.

Methane and Hydrogen. (*a*) ***Hinman's Method.***[39]—The gas left from the absorption of carbon monoxide is passed into the large explosion pipette. About half the requisite quantity of oxygen (40 ml.) necessary to burn the gas is now added, mercury introduced through the *T* in the connector sufficient to seal the capillary of the explosion pipette, all rubber connectors carefully wired, the pinchcocks closed, and the pipette cautiously shaken. *A screen of heavy glass or fine wire gauze* is interposed between the operator and the apparatus, the explosion wires are connected with the induction coil, a spark passed between them and the pinchcocks opened, sucking in the remainder of the oxygen. The capillary is again sealed with mercury, the stopcock opened and closed, to bring the contents of the pipette to atmospheric pressure, and the explosion repeated as before, and the stopcock opened.

It may be found expedient to increase the inflammability of the mixture, to introduce 5 ml. of " detonating gas," the electrolytic mixture of hydrogen and oxygen. The gas in the pipette containing carbon dioxide, oxygen, and

[37] Or cuprous sulfate (Reagents) may be used.
[38] Bull. Soc. Chim., **35**, 513; Abstr. Analyst, **31**, 349 (1906).
[39] Gill and Hunt, J. Am. Chem. Soc., **17**, 987 (1895).

nitrogen is transferred to the mercury burette and accurately measured. The carbon dioxide resulting from the combustion of the marsh gas is determined by absorption in potassium hydroxide; to show the presence of an excess of oxygen, the amount remaining is determined by absorption with potassium pyrogallate.

The calculation is given below. For very accurate work a second analysis should be made, making successive explosions, using the percentages of methane and hydrogen just found as a basis upon which to calculate the quantity of oxygen to be added each time. The explosive mixture should be so proportioned that the ratio of combustible gas (i.e., CH_4, H and O) is to the gases which do not burn (i.e., N and the excess of CH_4 and H) as 100 is to about 50 (from 26 to 64);[40] otherwise the heat developed is so great as to produce oxides of nitrogen, which, being absorbed in the potassium hydroxide, would affect the determination of both the methane and the hydrogen. The oxygen should preferably be pure, although commercial oxygen, the purity of which is known, can be used; the oxygen content of the latter should be tested from time to time, especially with different samples.

(*b*) ***Hempel's Method.***[41]—From 12 to 15 ml. of the gas are measured off into the burette (e.g., 13.2 ml.) and the residue is passed into the cuprous chloride pipette for safe keeping. That in the burette is now passed into the small explosion pipette; a volume of air more than sufficient to burn the gas, usually about 85 ml., is accurately measured and also passed into the explosion pipette, and in so doing water from the burette is allowed partially to fill the capillary of the pipette and act as a seal. The rubber connectors upon the capillaries of the burette and pipette are carefully wired on, both pinchcocks shut, and the stopcock closed. The pipette is cautiously shaken, the screen interposed, the explosion wires connected with the induction coil, a spark passed between them, and the stopcock immediately opened. The gas in the pipette, containing carbon dioxide, oxygen, and nitrogen, is transferred to the burette, accurately measured, by reading immediately, to prevent the absorption of carbon dioxide, and carbon dioxide and oxygen determined in the usual way.

Calculation. (*a*) ***Hinman's Method.***—56.2 ml. of gas remained after the absorption; 77.4 ml. of oxygen were introduced, giving a total volume of 133.6 ml.

Residue after explosion	46.9 ml.
Residue after CO_2 absorption	28.2 "
Carbon dioxide formed	18.7 "
Contraction	133.6 − 46.9 = 86.7 "
Residue after O absorption	25.6 "
Oxygen in excess	28.2 − 25.6 = 2.6 "

The explosion of marsh gas or methane is represented by the equation

$$\boxed{CH_4} + \boxed{O_2}\ \boxed{O_2} = \boxed{CO_2} + \boxed{H_2O} + \boxed{H_2O}.$$

From this it is evident that the volume of carbon dioxide is equal to the volume of methane present; therefore in the above example, in the 56.2 ml. of gas burned, there were 18.7 ml. methane.

[40] Bunsen, "Gasometrische Methoden," 2d ed., **73** (1877).
[41] Hempel, "Gas Analytische Methoden," 3d ed., 245 (1901).

The total contraction is due (1) to the disappearance of oxygen in combining with the hydrogen of the methane, and (2) to the union of the free hydrogen with oxygen. The volume of the methane having been found, contraction (1) as can be ascertained from the equation above, equals twice the volume of the methane; hence

$$86.7-(2\times 18.7)=49.3 \text{ ml.},$$

contraction which is due to the combustion of hydrogen. This takes place according to the following reaction: [42]

$$\boxed{H_2}+\boxed{H_2}+\boxed{O_2}=\boxed{H_2O}+\boxed{H_2O}.$$

Hydrogen then requires for its combustion half its volume of oxygen; hence this 49.3 ml. represents a volume of hydrogen with ½ its volume of oxygen, or 3/2 volumes; hence the volume of hydrogen is 32.9 ml.

(*b*) ***Hempel's Method.***—Of the 82 ml. of gas remaining after the absorptions, 13.2 ml. were used for the explosion; 86.4 ml. air introduced, giving a total volume of 99.6 ml.

Residue after explosion	78.0 ml.
Residue after CO_2 absorption	73.2 "
Carbon dioxide formed	4.8 "
Contraction	99.6−78.0=21.6 "
Residue after O absorption	70.2 "
Oxygen in excess	73.2−70.2= 3.0 "

The carbon dioxide being equal to the methane present, in the 13.2 ml. of gas burned there were 4.8 ml. of methane. The volume of methane is found by the proportion 13.2 : 82 : : 4.8 : x, whence $x=29.8$ ml.

The hydrogen is calculated similarly.

Another method for the estimation of hydrogen is by absorption with palladium sponge; [43] it, however, must be carefully prepared, and it is the author's experience that one cannot be sure of its efficacy when it is desired to make use of it. A still better absorbent of hydrogen [44] is a 1% solution of palladous chloride at 50° C.; when fresh this will absorb 20–50 ml. of hydrogen in ninety minutes. A proportionately longer time is required if more hydrogen be present or the solution nearly saturated. The methane could then be determined by explosion or by mixing with air and passing to and fro over a white-hot platinum spiral in a tubulated pipette called the grisoumeter [45] (grisou = methane).

Nitrogen.—There being no direct and convenient method for its estimation with this apparatus, the percentage is obtained by finding the difference between the sum of all percentages of the gases determined and 100%.

New [46] determined nitrogen in illuminating gas directly after the method of Dumas in organic substances; 150 ml. of gas are used, the hydrocarbons par-

[42] H_2O being as steam at 100° C. At ordinary temperatures this is condensed, giving rise to "total contraction."

[43] Hempel, Berichte, **12**, 636 and 1006 (1879).

[44] Campbell and Hart, Am. Chem. J., **18**, 294 (1896).

[45] Winkler, Fres. Zeit., **28**, 269 and 288.

[46] J. Soc. Chem. Ind., **11**, 415 (1892).

tially absorbed by fuming sulfuric acid and the remainder burned in a combustion tube with copper oxide; the carbon dioxide is absorbed and the residual nitrogen collected and measured.

Accuracy and Time Required.—For the absorptions the apparatus is accurate to 0.1 ml.; for explosions by Hinman's method [47] the methane can be determined within 0.2%, the hydrogen within 0.3%; by Hempel's method within 1% for the methane and 7.5% for the hydrogen. The time required by the student for the analysis of city gas is from three to three and one-half hours; for air, from fifteen to twenty minutes. For very accurate work the apparatus of Burrell should be used.

NOTES.—The object in filling the capillaries of the explosion pipettes with water or mercury before the explosion is to prevent the bursting of the rubber connectors on them. With mercury this is effected by introducing it through the *T*-joint in the connector. After testing for oxygen with the pyrogallate a small quantity of dilute acetic acid is sucked into the burette to neutralize any alkali which by any chance may have been sucked over into it. The acid is rinsed out with water and this is forced out by mercury before the burette is used again.

For results of the highest degree of accuracy the following points must be borne in mind.

1. The burette must be calibrated.
2. The confining liquid in the burette must be saturated with gas.
3. The reagents must be saturated with the gases for which they are *not* the reagent: a blank analysis should be run when the pipettes are first filled.
4. The reagents must be capable of absorbing their intended gases, i.e., not be nearly exhausted.
5. Check readings must be obtained after allowing the burette to drain 2 minutes.
6. Make sure connectors are tight, glass tubes close together, and that too great differences in the leveling tube and burette are not suddenly applied.
7. The ratio of combustible to non-combustible gases should not be less than 1 : 6. For safety the explosion pipette *must be screened.*

The method of analysis of the residue after the absorptions have been made by explosion is open to two objections: 1st, the danger of burning nitrogen by the violence of the explosion; and 2d, the danger of breakage of the apparatus and possible injury to the operator. These may be obviated by employing the apparatus of Dennis and Hopkins,[48] which is practically a grisoumeter or slow combustion pipette with mercury as the confining liquid; or that of Jaeger,[49] who burns the gases in a hard-glass or quartz tube filled with copper oxide. By heating to 250° C. nothing but hydrogen is burned; if the temperature be carried to 300°±10° and CO be present, both it and hydrogen can be burned, and from the CO_2 formed, the amount of CO determined, thus saving the time-consuming absorption; higher heating of the residue burns the methane. The air contained in the tube can be determined as in the case of the tube containing iodic anhydride, page 2356.

To the method of explosion by the mixture of an aliquot part of the residue with air, method (*b*), there is the objection that the carbon dioxide formed is measured over water in a moist burette, giving abundant opportunities for its absorption, and that the errors in analysis are multiplied by about six, in the example by 820/132.

[47] Cill and Hunt, loc. cit.
[48] J. Am. Chem. Soc., **21**, 398 (1899).
[49] J. Gasbeleuchtung, **41**, 764. Abstr. J. Soc. Chem. Ind., **17**, 1190 (1898).

THE PROPERTIES OF THE VARIOUS GASES AND THE METHODS OF THEIR DETERMINATION

Group I—Gases soluble in H_2SO_4, 1.7 sp.gr. Ammonia, Nitrous anhydride, Nitrogen tetroxide (also traces of propane, butane, propene and butene).

Ammonia was studied by Priestley in 1774, who named it "alcaline air." Ammonia is a pungent, strong smelling gas, lighter than air, specific gravity about 0.6 [50] (air being 1), dissolving readily in water, giving an alkaline solution. It is the *most soluble* gas, water dissolving about 700 volumes [50] at ordinary temperature (20°). Alcohol dissolves 340 volumes, and ether dissolves 10 volumes at 15°. Liquid ammonia has been an article of commerce for many years, being used in the refrigeration industry. At ordinary temperature liquid ammonia exerts a pressure of about 125 lbs. per sq. inch (8.5 atmospheres) and it boils at −33.5°. The capacity and sizes of the cylinders in which it is sold are given in the Appendix, Table 8.

Cylinders containing liquefied gases must be stored in a cool place and must not be handled roughly. They must be treated like a high explosive—as some of them are—the writer knowing of several cases in which casualties and deaths even have resulted from thoughtless handling. In handling ammonia the canister of the gas mask is filled with cupramite.[51] When inhaled none of the gas is absorbed,[52] the effect being entirely on the surface: 0.04% irritates the throat and 0.3% is dangerous for short exposure.

Ammonia burns with a yellow flame with pure oxygen, it is explosive with air, the explosive limits being from 16.5 to 26.8%.[53] Accidents in refrigerating plants have occurred from this cause.[54] From its high hydrogen content it behaves like hydrogen, reducing the oxides of the metals. It is decomposed by the electric spark into its elements. The source of ammonia was the distillation of coal,[55] but at present it is synthesized, using pressures of about 200 atmospheres and a temperature of 450° with a catalyst of iron and traces of other metals. In nature it is formed by the decomposition of protein, giving the "albuminoid ammonia" and "free ammonia" of the water analyst. These in turn are oxidized to nitrites and nitrates, forming the nitrogen cycle.

Qualitative detection is by the white fumes produced by strong hydrochloric acid, and by the odor.

Quantitative determination: by (*a*) absorption in water or standard acid and subsequent titration, cochineal often being used as an indicator, Table 9. (*b*) In the case of tarry or highly colored solutions, an apparatus like the nitrometer, p. 2418, may be used and the solution treated with sodium hypobromite, when a molecule of nitrogen is evolved for every 2 mols of free ammonia present.

$$2NH_3+3NaBrO=N_2+3NaBr+3H_2O.$$

[50] For accurate figures see Appendix, Table 3.

[51] Cupramite is a mixture of 1.5 parts 8–14 mesh pumice with 1 part $CuSO_4$, $5H_2O$; 45 cu. in. will protect against 2% ammonia for 5 hours.

[52] Henderson and Haggard, "Noxious Gases."

[53] Refrigerating Engineering, **17**, 65 (1929). J. Gasbeleuchtung, **57**, 941 (1914).

[54] Power, **72**, 128 (1930).

[55] Ammonia is formed when very dilute nitric acid acts upon zinc.

Or the gas may be strained through cotton, and passed into 10% sulfuric acid in the familiar gas washing bottles, 5 to 10 cubic feet of gas being used.

The acid is transferred to an ammonia distillation apparatus, as that of Kjeldahl, the contents made alkaline with sodium hydroxide, distilled into standard acid and titrated with standard alkali. The distillation is continued until the steam from the still does not change turmeric paper. (*c*) By Nessler's solution. This is a solution of mercuric iodide in potassium iodide, made strongly alkaline with potassium hydroxide which gives a yellow red coloration with ammonium compounds: this is matched in tubes with colors produced by standard solutions of ammonium chloride. The process is rapid and very delicate, one part nitrogen as NH_3 being detected in 1 billion parts of water. It is particularly used in water analysis.

Nitrous Anhydride N_2O_3 according to some authorities does not exist. It is very unstable and behaves like a mixture of nitrogen dioxide and nitric oxide.

Nitrogen dioxide, Nitrogen peroxide, NO_2, or Nitrogen tetroxide, N_2O_4 (cold).—Nitrogen dioxide is a reddish-brown acid gas heavier than air, of about 1.6 sp.gr. It is readily soluble in water forming nitric acid and nitric oxide, $H_2O+3NO_2=2HNO_3+NO$ (hot) and $N_2O_4+H_2O=HNO_3+HNO_2$ (cold). It is prepared by the heating of lead nitrate $2Pb(NO_3)_2=4NO_2+2PbO+O_2$: also by the action of concentrated nitric acid on copper or tin. At $-9°$ it is a white crystalline solid; at 26° a bright liquid; at 150° a deep brown gas.

On account of the high content of oxygen, nitrogen dioxide is an energetic oxidizing agent, carbon monoxide and phosphorus being oxidized by it. The dry liquid gas mixed with benzene, C_6H_6 or naphthalene $C_{10}H_8$ forms a powerful explosive when detonated, the products being wholly gaseous. It was used in depth bombs.

Physiological Action.—" Nitrous fumes " are intensely irritating to the respiratory tract, and are the most insidious of the irritant gases. After inhaling the fumes from the burning of dynamite, celluloid [56] or from action of nitric acid on metals or sawdust, one may be little inconvenienced and appear perfectly well. Before noon of the next day or even before the morning he may be dead, from the volume of liquid coming from the dropsy of the lungs; .011 to .015% is dangerous and twice this quantity rapidly fatal.

Qualitative detection—by means of iodo starch paper; or absorb in alkali and test for nitrates.

Quantitative determination—by absorption in standard potassium permanganate acidified with sulfuric acid.

$$10NO_2+2KMnO_4+3H_2SO_4+2H_2O=10HNO_3+K_2SO_4+2MnSO_4.$$

Allison, Parker and Jones [57] determined small quantities of " nitrous fumes " in the air by treating a known quantity of the gas with caustic soda solution, evaporating, and treating the residue with phenol sulfonic acid after the procedure for nitrates in potable waters.

[56] See Proceedings of a Board of the Chemical Warfare Service, etc. which investigated the disaster at the Cleveland Hospital Clinic, Cleveland, Ohio, May 15, 1929.

[57] Bur. Mines Tech. Paper 249 (1921).

Group II—Gases soluble in KOH, 1.3 sp.gr. Chlorine, Hydrochloric acid, Cyanogen, Hydrocyanic acid, Hydrogen sulfide, Sulfur dioxide, Silicon fluoride, and Carbon dioxide.

Chlorine was discovered by Scheele in 1774, who named it " Dephlogisticated marine acid air; " [58] Davy called it chlorine in 1810. Chlorine is a greenish yellow, stifling gas, about 2.5 times as heavy as air, dissolving readily in water to the extent of about twice its volume at 20°.[59] Liquid chlorine boils at −33.6° and at 20° exerts a pressure of 97 lbs. per sq. in. (6.6 ats.). It has been an article of commerce for many years, and is now shipped in tank cars.

Chlorine is the most active gas except fluorine: it attacks the metals and substances containing hydrogen, combining with it, decomposing them, destroying evil smells and colors—hence its use as a disinfectant and bleaching agent. Brought in contact with water the following equation takes place: $H_2O+Cl_2=HOCl+HCl$. The hypochlorous acid, HClO decomposes, $2HClO=2HCl+O_2$ and the " nascent " oxygen really is the active agent, rather than the chlorine. But this reaction also takes place, $H_2S+Cl_2=2HCl+S$. As a bleaching agent, where it can be used, chlorine is much more effective than some others, as sulfurous acid. Passed into caustic potash it forms hypochlorite or chlorate according to the temperature, the equations being $2KOH+Cl_2=KClO+KCl+H_2O$ and $6KOH+3Cl_2=5KCl+KClO_3+3H_2O$. Chlorine when passed into water at 0° forms a crystalline hydrate $Cl_2, 8H_2O$ which when heated yields the pure (hydrous) gas.

Chlorine finds many and important uses—in bleaching, and the preparation of organic compounds, as war gases, carbon tetrachloride (pyrene), chloroform, and the chlorides of the elements generally.

Chlorine is made chiefly by the electrolysis of brine, caustic soda being an important by-product. Where the Leblanc soda process is still employed, it is made as did Scheele by the oxidation of hydrogen in hydrochloric acid with manganese dioxide, $4HCl+MnO_2=MnCl_2+Cl_2+2H_2O$.

Physiological Action.—Chlorine produces irritation of the tissues, probably by their oxidation, as has already been explained in the case of bleaching: .0015% irritates the throat and .004% is dangerous; 0.1% is fatal.

Chlorine can be removed from hydrochloric acid gas by treatment with powdered antimony.

Hydrochloric acid (hydrogen chloride) was prepared by the alchemist Geber in 1648, and in the anhydrous condition by Priestley in 1772, who called it " marine acid air." It is a colorless gas, heavier than air (sp.gr. 1.25), strongly acid, and fumes when brought in contact with moisture. It is a remarkably stable gas, requiring a temperature of 1600° to 1800° for its decomposition; at this temperature it burns with oxygen. It is the second most soluble gas, water at ordinary temperatures dissolving 450 volumes:—an aqueous solution containing 20.24%, distils at a constant temperature of 110° at 760 mm. Alcohol gives a 40% solution, it is also soluble in ether and hydrocarbons. It has been condensed to a liquid having a pressure of 42 atmospheres at 18° (620 lbs.).[60]

[58] I.e., "marine acid" (HCl) from which the phlogiston (H) had been removed.

[59] Accurate figures in Table 3.

[60] The liquid gas is contained in a tube 5.5 mm. internal diameter and 1 mm. thickness of wall, which gives an idea of the pressure such tubes may be expected to withstand.

Qualitative detection: by the dense white fumes with ammonia.

Quantitative determination: by absorption in standard alkali or silver nitrate.

Hydrochloric acid can be removed from chlorine by passing the gas over manganese dioxide or zinc oxide.

Cyanogen or dicyanogen, C_2N_2, was discovered by Gay Lussac in 1815, and is made by heating mercuric cyanide: $Hg(CN)_2 = Hg + C_2N_2$. It is a poisonous, colorless gas with an odor resembling prussic acid, heavier than air (sp.gr. 1.8): it burns with a purplish flame, when liquefied it has a pressure of 73.5 lbs. (5 atmospheres) at 20°. At this temperature one volume of water dissolves 4.5 volumes of the gas. Alcohol dissolves 23 volumes and ether 5, in which it decomposes very slowly. The aqueous solution turns dark, precipitates brown flakes, and contains a quantity of nitrogenous compounds, as oxamide, prussic acid and urea.

Cyanogen is most readily prepared by heating the mixed concentrated solutions of potassium cyanide and copper sulfate.

Qualitative Detection and Quantitative Determination.—By solution in caustic soda and testing for cyanide. $C_2N_2 + 2KOH = KCN + KCNO + H_2O$. Cyanogen may be determined by Nauss' method [61] consisting in its absorption in ferrous hydroxide or in presence of hydrocyanic acid by Rhodes method [62] by absorption in silver nitrate: this precipitates the acid and the cyanogen can be separated by drawing air through the solution. Another method consists in absorbing in alkali hydroxide acidifying with acetic acid, adding a few drops of copper sulfate (1 : 10), a drop or two of pyridine, and 5 ml. of chloroform. A blue coloration in the chloroform layer indicates a cyanate—which is not given by a cyanide. The following equations serve to distinguish between the gases:

$$C_2N_2 + 2H_2O + (HCl) = \begin{matrix} CONH_2 \\ | \\ CONH_2 \end{matrix} + (HCl) \text{ oxamide,}$$

$$HCN + 2H_2O\ (HCl) = HCOOH + (HCl) + NH_3 \text{ Formic acid.}$$

Hydrocyanic Acid or Prussic Acid HCN was prepared by Scheele in 1782. It is easily made by treating potassium or sodium cyanide with sulfuric acid 1 : 1. It is a colorless mobile liquid of a boiling point of 25.7°, having a peculiar odor resembling bitter almonds. The characteristic odor of potassium cyanide is due to this gas, being such a weak acid that it is displaced by the carbonic acid of the air. The gas is lighter than air (sp.gr. 0.93) and is one of the most powerful and rapid poisons. It is readily soluble in water, alcohol and ether. Both the liquid gas and the concentrated aqueous solution are readily inflammable, burning with a violet flame.

Hydrocyanic acid has of late years found important use as an insecticide, particularly against the scale insects infesting citrus groves, and for fumigating storage warehouses for grains and furniture.[63] It is made by the action of sulfuric acid upon sodium cyanide and in California the 97% acid is shipped in

[61] J. Gasbeleuchtung, **43**, 696 (1900).
[62] Ind. Eng. Chem., **4**, 652 (1912).
[63] "The Modern Miller," Feb. 1927; The Furniture Warehouseman, **6**, May (1926); Pacific Marine Review, Nov. 1926.

tinned iron drums;[64] in 1926 Metzger[65] discovered that acid calcium cyanide $Ca(CN)_2 \cdot 2HCN$, gives off three-fourths of the acid in half a minute and the whole of it in a minute. It is extremely sensitive to moisture: $CaH_2(CN) + 2H_2O = Ca(OH)_2 + 4HCN$. It is known as "powdered hydrocyanic acid."

Physiological Action.—Cyanides or cyanogen arrest oxidation in the tissues and produce asphyxia. The person falls after a few breaths of the polluted atmosphere and dies in 6 to 8 minutes. 0.012% is dangerous and 0.3% rapidly fatal. Ammonia and chlorine are the antidotes. Like "nitrous fumes," it is evolved when celluloid burns.

Qualitative Detection and Quantitative Determination.—By absorption in water or standard alkali, and testing for a cyanide: or it may be absorbed in standard silver nitrate, or converted to a ferricyanide.[66]

Cyanogen compounds are formed whenever nitrogenous and carbonaceous compounds come together at high temperatures, particularly if alkali be present. They are found in blast furnace, coal and destructor gases.

Hydrogen Sulfide H_2S was carefully investigated by Scheele, who synthesized it from its elements. It occurs in the natural gas of certain Texas localities to the extent of 20%,[67] and in "sulfur springs." It is a colorless gas of well known odor, a little heavier than air (sp.gr. 1.18), boiling at $-62°$: at 20° the liquid gas exerts a pressure of about 150 lbs. per sq. in. (10 atmospheres). It is readily decomposed—hence a good reducing agent; it is combustible, explosive limits 4.3–46.0%, and soluble in water to the extent of 3 ml. per ml. of water at 20°,[68] alcohol dissolves about 7 volumes. The usual method of preparation from ferrous sulfide gives a gas containing hydrogen (40% in some cases) from the excess iron. For the preparation of the pure gas, a pure sulfide, as Stibnite, should be employed.

Physiological Action.—Sulfuretted hydrogen is nearly as toxic as prussic acid, and its action may be as rapid. It is a non-cumulative poison, is rapidly oxidized by the blood and its products are non-toxic; 0.01–0.015%, may produce death in from 8 to 48 hours.[69] .05 to .07% is dangerous and 0.1 to 0.3 rapidly fatal.[70]

Qualitative detection by "lead paper," i.e., filter paper moistened with a solution of lead acetate giving a black or brown coloration.

Quantitative Determination.—It can be absorbed in a standard solution of iodine in potassium iodide. Small quantities can be determined colorimetrically by p-amino dimethyl aniline sulfate.[71]

Hydrogen sulfide can be separated from carbon dioxide, hydrogen and hydrocarbons by powdered manganese dioxide.

Sulfur Dioxide SO_2—was first prepared in the pure state by Priestley in 1775, by the action of sulfuric acid on mercury, as the result of the breaking of a thermometer in distilling the acid. It is a colorless gas of suffocating odor, a

[64] Ind. Eng. Chem., **25**, 959 (1933).
[65] Id., **18**, 161 (1926).
[66] Rhodes, Ind. Eng. Chem., **4**, 652 (1912).
[67] Bur. Mines Reports of Investigations, No. 3128 (1931).
[68] The solution saturated at 0° contains 4.3 ml. per ml. of water, and used as a gargle or spray, is almost a specific cure for tonsilitis.
[69] Yant and Sayers, J. Chem. Ed., **4**, 613 (1927).
[70] Haggard, Chem. Abstr., **19**, 2095 (1925).
[71] Sheppard and Hudson, Ind. Eng. Chem., Anal. Ed. **2**, 73 (1930).

little more than twice as heavy as air (sp.gr. 2.2), readily soluble in water, 1 ml. dissolving 40 ml. at 20°,[72] alcohol dissolves 32%. At this temperature the liquid exerts a pressure of 48 lbs. per sq. in. (3¼ atmospheres). It boils at −10°. It is an energetic reducing agent but a very stable gas. It is particularly harmful to vegetation, especially conifers. Three to 4 parts per million injure the leaves of plants after one hour exposure.[73] Therefore it is recommended that in works where it is used, or in chemical works in general, that well authenticated, clear and dated photographs of the surroundings—particularly with reference to arboreal or plant damage—be made from time to time.

Physiological Action.—It is said to cause decomposition of haemoglobin, inflammation, and irritation of the respiratory tract may occur. Acute poisoning from the gas is rare, on account of the sensitivity of the eyes and throat to it—it being the gas which is most easily perceptible. .0008% irritates the throat and .04% is dangerous.

Qualitative determination—by the bleaching of fuchsin paper or iodo-starch paper.

Quantitative determination—in standard iodine solution [74] $SO_2+2I+2H_2O=H_2SO_4+2HI$. This is the method given on p. 2399. Sweeney, Outcault and Withrow [75] advocate the use of .005 N permanganate; or by absorption in standard alkali.[76] See also the report of the Selby Smelter, Commission Bur. Mines. Bull. 98 (1915).

As has been stated, it is absorbed by zinc-filled rubber tubing.[77]

Silicon fluoride or **tetrafluoride** was discovered by Scheele in 1771 and investigated by Berzelius in 1823. It is a colorless gas fuming strongly in the air, of odor resembling hydrochloric acid: It has a specific gravity of 3.6. It is readily decomposed by water, precipitating silicic hydroxide, $3SiF_4+4H_2O=Si(OH)_4+2H_2SiF_6$. It has been liquefied—the liquid is said to have a tension of 50 lbs. (3.4 ats.) at 20°. It is formed when hydrofluoric acid acts upon silica or silicates:

$$4HF+SiO_2=SiF_4+2H_2O.$$

Qualitative and quantitative determination—by the use of the decomposition with water.

Carbon Dioxide or Carbonic Acid, CO_2—was investigated by Bergman in 1774 who gave it the name of "acid of air." Lavoisier showed its chemical nature. It is a normal constituent of the air, present to the extent of 3 parts per 10,000. It is a colorless and odorless gas, 50% heavier than air (sp.gr. 1.5); but *hot* CO_2 at 150° for example, is lighter than air. Five to seven per cent mixed with oxygen [78] serve as a stimulant in artificial respiration, and a similar effect is observed with carbonated waters and wines. Three or 4% in the air is noticeable,[79] 6% produces panting, 7 to 8% more distress, increasing at 11%, 15% extinguishes lights, and 50% causes death, the action being the exclusion

[72] For accurate figures see Table 3.
[73] Zimmerman and Crocker, J. Chem. Ed., **8**, 1344 (1931).
[74] Bureau of Mines Bulletin 98.
[75] Ind. Eng. Chem., **9**, 949 (1917).
[76] Ind. Eng. Chem., **18**, 747 (1926).
[77] Power, **58**, 507.
[78] Henderson, Science, **83**, 402 (1936).
[79] Haldane, Am. Gas Lt. J., **65**, 483.

of oxygen. It is a remarkably stable gas, requiring a very high temperature —2000°—for its decomposition. Water at ordinary temperature dissolves its own volume of the gas; at a pressure of 3 to 4 atmospheres it becomes "soda water" [80] of commerce. Liquid carbonic acid evaporates at −79° and the solid melts at −56°. It has no boiling point. At 20° it exerts a pressure of 870 lbs. (59 atmospheres). From a cylinder of the compressed gas when opened the gas escapes as a snow-like solid. This is compressed at a pressure of 500 to 800 pounds per sq. in., into cakes known as "dry ice," [81] dissolved in acetone it is a very convenient method of producing low temperatures in the laboratory.

Qualitative detection by calcium or barium hydroxide on an ebonite rod.

Quantitative Determination.—By standard alkali or absorption in sodium or potassium hydroxide and noting contraction in volume. Scheibler's calcimeter is an ingenious apparatus, in which carbon dioxide evolved from bone charcoal (containing calcium carbonate) and acid displaces an equal volume of air from a rubber bag inside a Woulff bottle, into a burette. The burette is graduated in per cent of calcium carbonate, 1.7 grams of bone char being taken.

Carbon dioxide has of late found estended use: with a peculiar nozzle, the liquefied gas serves as a fire extinguisher, as a source of decentralized power for spray painting, unplugging pipes, distilling tar and petroleum and displacing flammable solvents and oil vapors in tankers. Used aboard ship as a refrigerant.[82] It may, if the percentage be high, cause the development of objectionable flavors [83] with fresh fruits and vegetables, for these carry on respiration. The solid gas compressed into bricks has replaced ice to a considerable extent. It is said to be used also as a rat-killer and tire inflater.

Carbon dioxide in illuminating gas cuts down the illuminating power almost in the proportion to which it is present.

Group III—Gases Soluble in $AgNO_3$ Solution.—Phosphine PH_3, Arsine AsH_3, Stibine SbH_3.

These gases are all poisonous, readily decomposed with the liberation of hydrogen, form chlorides, are all combustible and decompose explosively. They all combine with silver when passed into silver nitrate, setting free nitric acid. This acts upon the precipitated silver compound forming phosphoric or arsenious acid; this does not take place with stibine, $PH_3+3AgNO_3=Ag_3P+3HNO_3$. They are not commonly met with except as impurities in other gases.

Phosphine PH_3 was prepared by Gengembre in 1783 by heating phosphorus with potassium hydroxide, giving at the same time a liquid P_2H_4, which is spontaneously inflammable. $3KOH+4P+3H_2O=PH_3+KH_2PO_2$. As ordinarily encountered, phosphine smells like rotten fish and comes from the decomposition of the metallic phosphides by acid. The pure gas inflames above 100° and it takes fire when treated with nitric acid or bromine. It is somewhat

[80] It is interesting to note that perhaps Cleopatra made the first carbonated drink, when she dissolved a valuable pearl in vinegar. Dr. P. C. Physick of Philadelphia prescribed soda water as a medicine in 1807, which was put up by Townsend Speakman. It became very popular, and in 1928 the annual business in carbonated drinks amounted to 800 million dollars.

[81] Killeffer, Ind. Eng. Chem., **19**, 192 (1927).

[82] Power, **67**, 805 (1928).

[83] Thornton, Ind. Eng. Chem., **22**, 1186 (1930). Brooks, Power, **67**, 805 (1928).

heavier than air having a specific gravity of 1.18. It is very slightly soluble in water, 100 ml. dissolving 2.6 ml. Alcohol dissolves about half its volume, and ether twice its volume. *Qualitative detection*—by the blackening of silver nitrate solution in the absence of hydrogen sulfide and the other members of this group.

Quantitative determination—by converting to phosphoric acid by burning, after the manner of the determination of sulfur in city gas (p. 2395) and subsequent oxidation with bromine and precipitation of the phosphoric acid as magnesium phosphate in the usual way. Dennis and O'Brien [84] recommend the determination in acetylene by absorption in sodium hypochlorite and ultimate precipitation as magnesium phosphate: wt. $Mg_2P_2O_7 \times 0.3059 = $ wt. PH_3 or wt. $Mg_2P_2O_7 \times 201.25 = $ ml. PH_3.

Arsine, AsH_3, was discovered by Scheele in 1775, who prepared it by heating a solution of arsenic acid with zinc. It is evolved when acids act upon arsenical metals. It is a colorless gas of disagreeable odor, extremely poisonous,[85] easily decomposed by heat and readily inflammable. It is 2.7 times as heavy as air; water dissolves 1/5 its volume of the gas, it is insoluble in alcohol and ether; it liquefies at $-55°$.

When inhaled it produces dizziness, faintness and headache, followed by nausea and vomiting; it combines readily with hemoglobin, producing anemia. In acute cases death ensues in from 2 to 6 days.

Qualitative detection—by passing into ammoniacal silver nitrate.

Quantitative determination—by the familiar Marsh test; also by the Gutzeit [86] test: $2AsH_3 + 12HgCl_2 + 3H_2O = 12HgCl + As_2O_3 + 12HCl$; the calomel can be weighed, or potassium iodide solution is added sufficient to dissolve it; 25% excess iodine solution added, and the excess iodine titrated with N/100 thiosulfate: 1 mg. $As_2O_3 = 8.08$ ml. N/100 thiosulfate.

Stibine, SbH_3, was prepared by Lewis Thompson in 1837; it is formed whenever " nascent " hydrogen comes in contact with a soluble antimony salt. It is a colorless gas, of odor faintly resembling hydrogen sulfide, inflammable, easily decomposed by heat or even strong sulfuric acid. It is more than four times as heavy as air, of boiling point $-17°$, and is soluble in water to the extent of 1/5 its volume, 1 ml. alcohol dissolves 15 ml.

Determination—by passing into silver nitrate, forming $SbAg_3$, washing and dissolving in tartaric acid and determining the antimony.

Group IV—Gases soluble in potassium pyrogallate.

Oxygen, the active constituent of the air, was known to the Chinese in the eighth century; they even knew it could be made by heating saltpeter: [87]

[84] Ind. Eng. Chem., **4**, 834 (1912).

[85] It is stated that Gehlen lost his life in 1815 by the inhalation of a single bubble of the gas.

[86] Barnes and Murray, Ind. Eng. Chem., Anal. Ed., **2**, 29 (1930).

[87] This fact is made use of periodically, to foist upon an unsuspecting public the various "coal savers" and "aids to combustion," to "burn up the noxious gases of combustion, and safeguard the health of the family." They do contain a little Chili saltpeter, sometimes permanganate, but their chief constituent is usually common salt. This colors the slightly visible flames of carbon monoxide, so that the combustion appears to be energetic, and the furnace very hot. Two pounds are sufficient to treat a ton of coal. When it is remembered that about 2 pounds of *oxygen* are required to burn a *single pound* of coal, it will readily be seen how much influence this compound will have in burning a *ton* of coal!

Mayow in 1669 found the percentage in the air, but it remained for Scheele in 1771–2, and in 1774, Priestley, to prepare it in a pure state. They called it the "vital spirit" or "fire air." It is prepared today commercially by the distillation of liquid air and the electrolysis of water. It is evolved by green plants, particularly under the influence of sunlight, with the formation of cellulose, $6CO_2+5H_2O=C_6H_{10}O_5+6O_2$. This is perhaps the most important reaction taking place in the world—the carbonic dioxide evolved by combustion and animals, being utilized by the plants for their sustenance, and they in turn contribute oxygen for ours.

Oxygen is 10% heavier than air, and at ordinary temperatures a liter of water dissolves 6.4 ml. of oxygen from the air, or 28.4 ml. from pure oxygen. It dissolves to the extent of 10 volumes in molten silver, which when cooled suddenly evolves it, "the spitting of silver," causing losses sometimes in assaying. It is colorless, odorless and tasteless. It was liquefied in 1877, becoming a steel blue liquid, and boiled at $-182.5°$ (nitrogen $-195.5°$). It comes in commerce in 110 and 220 cu. ft. cylinders under a pressure of 1800 lbs. per sq. in. at ordinary temperature.

If the atmosphere contains less than 17% oxygen oil lamps refuse to burn, at 16% gas does not burn, at 12% respiration becomes deeper, at 10% respiration becomes more difficult; the lips become blue, 8% the face is leaden color, and at 5 to 6%, panting and death ensue.[88]

Compressed oxygen is one of the commonest gases of today. The cylinders are provided with right-hand threads, whereas all the combustible gas cylinders have left-hand threads, and are served by oil lubricated pumps. "*Never put oxygen into a cylinder with a left-hand thread*"—is one of the cardinal principles to be observed in handling compressed gases. It is a "dangerous or hazardous material," particularly in contact with oil, even in minute quantities, as little as 0.6 mg. (1/50 drop) causing fire in the presence of high pressure oxygen.[89] Four drops of oil, in a 60 ml. bomb under a pressure of 2300 pounds causes an explosion.[90] In a case which the writer investigated, 1800 pounds pressure when exerted nearly 24 hours, blew a 220 ft. cylinder of compressed oxygen to pieces, caused the death of two persons, and wreckage of the laboratory; the floor above was blown up with such violence as to break the legs of persons standing upon it; windows were broken two hundred feet away. The amount of oil of course could not be determined, but other cylinders from the same lot contained from 50 to 100 mgs. of mineral oil: they were all intended for combustible gases, but as they were new and supposedly never used, they were temporarily used to hold oxygen, a special fitting being made for the purpose.

Cases are known in which people have been burned, and iron fittings set fire by incautious oiling, as firewood is kindled by kerosene. Water is the only lubricant to be used on an oxygen compressor, with a trace of soap in it for the fittings. Packings are of lead, asbestos or "nearly incombustible rubber." Iron or steel should not be used for fittings for high pressure oxygen. A verdict of $340,000 [91] was awarded, due to a fire caused by oil in a steel manifold, even

[88] Burrell and Oberfell, Bur. Mines Tech. Paper 122 (1915).
[89] News Edition of Ind. Eng. Chem., **2**, 6 (Dec. 20, 1924).
[90] Hersey, C. A., **17**, 3254 (1923). Also Brooks, C. A., **18**, 905 (1924).
[91] News Edition, Ind. Eng. Chem., **2**, 6 (Dec. 20, 1924).

though it was made in conformity with current practice. Brass or bronze fittings must be used—these melt but do not fire or burn.[92]

Used with compressed hydrocarbon gases or gasoline it finds extensive employment in cutting and welding iron and steel; this has developed an extensive technique and literature. It is to be noted that much depends upon the purity of the oxygen, both as regard the time consumed and the quality of cut produced. If 99.3% of oxygen or better, be regarded as standard, using hydrogen, a drop of a single per cent in purity increases the amount used by 25%, and the time by 7%; a drop to 95% purity makes a ragged cut, increases the time by 40% and the quantity of gas used by 60%.[93] The temperatures attained are 1800° with manufactured or illuminating gas, 2100° with hydrogen and 2450° with acetylene.[94]

Qualitative detection—by the familiar glowing splinter or by the passage of the gas into nearly colorless pyrogallate of potassium. This can be prepared by using well boiled water to dissolve the hydroxide and acid and mixing them out of access of air.

Quantitative Determination.—In case combustible gases are absent, by explosion with hydrogen (p. 2355); otherwise absorbents as phosphorus or potassium or sodium pyrogallate is used; this with much oxygen may evolve CO. See Reagents. Phosphorus does not absorb pure oxygen; if the concentration be reduced to 75% they combine with explosive violence. Burrell uses a stabilized solution of chromous chloride called " oxsorbent " with success; another excellent absorbent when carbon monoxide and acetylene are absent, is ammoniacal cuprous carbonate or chloride. This is prepared by treating bits of copper or copper gauze, cleaned with nitric acid, with 500 ml. of a saturated solution of ammonium carbonate mixed with an equal quantity of ammonium hydroxide, sp.gr. of 0.96. Badger [95] recommends treating the copper with a solution of equal parts of concentrated ammonia and water, saturated with ammonium chloride; this absorbs from 50 to 60 times its volume of oxygen.

Oxygen should not contain more than 4% of hydrogen and preferably none at all, and for respiration be of the highest quality containing not more than 2% impurities.

For the determination of oxygen dissolved in water the method of L. W. Winkler [96] is employed; the quantity of dissolved oxygen is usually a measure of the purity of the water.

Ozone O_3, van Marum observed in 1785 that when frictional electric machines were operated, a peculiar odor was developed at the same time; a similar odor was observed by the passage of a lightning spark. Little attention was paid to this until Schönbein brought it to the attention of chemists in 1840. He and others investigated it and found it not to be an oxide of hydrogen as was thought, but a form of oxygen. The investigation was a difficult one as the quantities of it formed were small and being so active it disappeared.

The odor resembles dilute chlorine; it is faintly blue in layers of a meter thick, and about 60% heavier than air; it is one of the most powerful oxidizing

[92] Jakowsky and Butzler, C. A., **17**, 3920 (1923).
[93] Circular International Oxygen Co., 1911; also J. Soc. Chem. Ind., **30**, 779 (1911).
[94] Drews, "Verdichtete und Verfluessigte Gase" (1928).
[95] Ind. Eng. Chem., **12**, 161 (1920).
[96] Ind. Eng. Chem., **5**, 976 (1913); also C. A., **7**, 2266 (1913).

agents; 1 ml. of water at 12° dissolves 0.5 ml. ozone. It forms a blue liquid boiling at −119° and is an endothermic compound.

Qualitative Detection.—Ozone browns manganese chloride paper and liberates iodine from potassium iodide. It does not affect permanganate as do hydrogen peroxide and " nitrous fumes." It of course does not respond to the nitrite test with sulfanilic acid and alpha naphthylamine as do " nitrous fumes " (N_2O_3 and NO), nor is it changed by chromic acid as is hydrogen peroxide. It turns silver foil black which neither of the others affects.[97]

Quantitative Determination.—By the action upon a *neutral* solution of potassium iodide, and titration of iodine with N/10 thiosulfate.[98] $2KI+O_3+H_2O=2KOH+2I+O_2$. If an acid solution be used, hydrogen peroxide is formed, which sets free an additional quantity of iodine. For the rapid determination of ozone in the air of health resorts use may be made of the Wurster [99] test, the quantitative oxidation of *fresh* p-tetramethyl phenylene diamine which forms a blue color on strips of paper which may be matched with standards.

Ozone is formed when oils, as turpentine, oxidize, or during the operation of blast lamps. It is used industrially for, " killing odors," oxidizing and bleaching oils, waxes, ivory, flour and starch; it has been used for purifying water, but chlorine is said to be cheaper—that, however, produces a taste. Great hopes were entertained for ozone when it was first made in quantity, that it could be used for improving the ventilation of halls and schoolhouses; the fact that the atmosphere was too dry for its efficient use was overlooked, and little effect resulted other than the production of sore throats for those in the immediate neighborhood of the machine.[100] In handling ozone, glass or metal apparatus must be used as it oxidizes all other materials. Flexibility of glass apparatus can be ensured by spirals or by the use of joints sealed with mercury cups.

Group V—Gas absorbed by Cuprous Chloride Solution.—Carbon Monoxide, CO.

It was obtained in 1776 by Lassone by heating zinc oxide with charcoal; this gave a gas which burned with a blue flame and which for a long time was mistaken for hydrogen. Cruikshank in 1800 found it could be made by heating various metallic oxides with carbon and named it " gaseous oxide of carbone." Its method of preparation industrially (with hydrogen) is by the well known water gas reaction; in the laboratory it can be made by the removal of water by sulfuric acid from formic acid or oxalic acid (with an equal volume of CO_2).

$$HCOOH=CO+H_2O; \qquad \begin{matrix} COOH \\ | \\ COOH \end{matrix} = H_2O+CO+CO_2.$$

If potassium ferrocyanide or cyanide be cautiously heated with 10 times its weight of *conc.* sulfuric acid, pure carbonic oxide is evolved (*dilute* acid gives

[97] Keiser and McMaster, Am. Chem. J., **39**, 96 (1908).
[98] Treadwell and Anneler, Z. Anorg. Chem., **48**, 86 (1905); also Treadwell-Hall, "Quantitative Analysis."
[99] Berichte, **20**, 921 (1888). Obtainable from T. Schuchardt, Goerlitz, Germany.
[100] Czaplewski, Chem. Met. Eng., **12**, 254. C. A., **8**, 2017 (1914).

hydrocyanic acid): $K_4Fe(CN)_6+6H_2O+6H_2SO_4=6CO+2K_2SO_4+FeSO_4+3(NH_4)_2SO_4$.

Carbon Monoxide is colorless, possessing a slight odor and taste. It is a trifle lighter than air, and has been liquefied, boiling point −190°; 100 ml. of water at 20° dissolve 2.3 ml., alcohol dissolves about 10 times as much. It is a stable gas, combining with chlorine to make the deadly phosgene $COCl_2$, with potassium to make the explosive $K_6C_6O_6$, and with nickel (cobalt), and iron to make the carbonyls $Ni(CO)_4$ boiling point 43°, and $Fe(CO)_5$—boiling point 102.5°. The latter occurs in city gas and deposits iron oxide on the gas mantles, injuring their efficiency. It is combustible, the explosive limits with air being from 12.5 to 75%. When heated with oxides of the metals it is a most powerful reducing agent, producing the metals. By its production from coal less than ⅓ the heating value of the carbon is evolved, 4340 B.t.u. instead of 14544 B.t.u. per pound.

Physiological Action and Common Sources of Carbon Monoxide—Sewer Gas.—When inhaled, carbon monoxide displaces oxygen from the blood by combining with the hemoglobin, the affinity for which is 300 times that for oxygen; consequently as the blood cannot be sufficiently oxygenated, the patient dies from asphyxiation. It acts too, as a cumulative poison, a little being taken into the system now and again until a toxic dose is attained. Coal gas contains 6 to 8%, water gas 25, producer 17 to 30, blast furnace 24, and automobile exhaust gases 7% carbon monoxide. No one would think of staying in a room into which coal gas was issuing from a one-inch pipe, and yet people stay in a garage with an automobile engine running, delivering more carbon monoxide than coal gas itself. A 30-horsepower engine running 15 minutes in a closed garage of 5000 cubic feet capacity will make the air decidedly dangerous.[101]

In the streets we find from 0.3 to 2.9 parts per 10,000; average 0.8 parts; [102] in auto repair shops from 0.1 to 11 parts, average 2.1 parts; in auto busses from 0.1 to 1.0 part. To get an idea of the danger, Henderson suggests that the number of parts of carbon monoxide in 10,000 be multiplied by the hours of exposure: if this product be 3 there is no effect, at 6 it is just perceptible, at 9, headache and nausea result, and if the concentration be 15, it is dangerous. In congested thoroughfares from 0.8 to 2.0 parts per 10,000 may be encountered, with the latter a headache may be expected after several hours exposure. 0.1% (10 parts per 10,000) produces loss of power over the lower limbs, 0.2% complete helplessness, and 0.3% (30 parts per 10,000) death; 10 ml. per kilogram weight of an animal will cause death, i.e., 800 ml. per person. When gassed "it is extremely important to hasten the elimination by inhalation of oxygen plus 5–7% carbon dioxide, and terminate the asphyxia." "A person who is allowed to recover spontaneously in fresh air may remain unconscious for some time and be ill a day or two, whereas another equally gassed, is resuscitated by inhalation, goes back to work within a half hour with no ill effects." [103]

[101] "Vitiation of Garage air by Automobile Exhaust Gases," Bur. Mines Tech. Paper 216 (1919).

[102] "Atmospheric Pollution by Automobile Exhaust Gases," Ind. Eng. Chem., News Edition, Aug. 20, 1928, p. 20.

[103] Henderson and Haggard, "Noxious Gases" already mentioned.

Sewer Gas.—Another source of carbon monoxide is " sewer gas," i.e., city gas which leaks into sewers, not *sewage gas*, coming from the fermentation of sewage in the sewers. This is unusual if not impossible, as the temperature of the sewage is such as not to favor fermentation, assuming that sewage collected in the sewers, which are inclined to ensure a sufficient flow to prevent accumulation. In long sewers of faulty construction and with stale sewage a gas having a high content of methane and no carbonic oxide might be produced. Gas leakage from mains under asphalt pavement was recognized in New York in 1897;[104] illuminating gas is found in electric manholes.[105] Cast iron pipes with bell and spigot joints, made with oakum and cement, are usually buried 30 inches, and present potential sources of leakage every 12 feet. The modern gasketted coupling and leak clamps have largely reduced this leakage. The normal leakage of a 6-inch main is 225 thousand cubic feet of gas per *mile* annually: a 12-inch main doubles this. This may mean from 7.1 to 25.9% of the gas made. In Massachusetts it is about 202 thousand cubic feet. City gas, therefore, may come into the house through defective plumbing or more likely it may follow from the trench containing the gas main along the service gas or water pipes or from electric ducts or conduits through the foundation walls into the house. Besides this source, carbon monoxide is formed wherever carbonaceous substances burn incompletely, even in manufactured gas, and particularly from charcoal braziers and coke burning stoves.[106] It is also formed by the explosion of smokeless powder, and occurs in gun turrets.

Qualitative detection—by the blood test or palladous chloride, pp. 2405–7.

Quantitative determination—by absorption in acid or ammoniacal cuprous chloride (see Reagents) each of which absorbs its own volume of the gas. The compound formed—possibly $2CuClCOH_2O$—is very unstable, as carbonic oxide may be freed from the solution by boiling, or placing it in vacuo: even if the solution containing it be simply shaken with an inert gas or one containing little carbonic oxide it is given off. Where mercury is the confining liquid, ammoniacal cuprous chloride should be used, as the acid chloride causes a troublesome flouring of the mercury. Cuprous chloride does absorb appreciable quantities of the higher paraffine hydrocarbons.

The compound of carbon monoxide and cuprous chloride, being so unstable, makes a very unsatisfactory absorbent for the gas. Two methods are in use to remedy the difficulty, by the use of cuprous sulfate and combustion with copper oxide. The compound formed with cuprous sulfate, Cu_2SO_4CO, is stable. It does not set free the gas, but acts more slowly than the chloride, particularly after it has become about half saturated. Whereas the chloride absorbs about its own volume, the sulfate absorbs 18 times as much. It absorbs the unsaturated, but not the saturated hydrocarbons, nor hydrogen, nitrogen, and only traces of oxygen.

By using first a cuprous chloride pipette until only a few cubic *millimeters* are absorbed, and finishing to complete absorption with a sulfate pipette, the analysis can be rapidly and accurately executed.

[104] Report of the National Board of Fire Underwriters, No. 559.

[105] "Gases in Manholes." U. S. Bureau Mines R. I. 3109 (1931); also R. I. 2710 (1925) and Rept. Investig. 3192, C. A., **26**, 6140 (1932); also White, C. A., **8**, 2914 (1914).

[106] Hoffman, "Considerations on the Fatal Effects of the Vapour from Burning Charcoal," 1716.

These absorption methods being slow, Burrell determines carbon monoxide and hydrogen together, by burning with copper oxide in a U-tube heated to 300°±12°: the CO_2 formed equals the CO present.

These methods are those ordinarily used for the estimation of considerable quantities of carbon monoxide: for the determination of small quantities using iodine pentoxide, see Analysis of Air.

Katz and Bloomfield [107] find that as little as 0.07% CO can be determined by "Hoolamite," a mixture of iodine pentoxide and fuming sulfuric acid on granular pumice stone. The mixture is kept in sealed glass tubes the ends of which are broken and connected up with a tube of activated charcoal through which the air to be tested is drawn by means of a measured rubber bulb. The amount of carbon monoxide is shown by comparing the color produced with a set of standards.

Group VI—Gas Soluble in Ferrous Sulfate Solution, 1 : 2.

Nitric oxide, NO, was discovered by Van Helmont and fully investigated by Priestley in 1772. It is a colorless gas, slightly heavier than air, has been liquefied—boiling point −153.6°, and very slightly soluble in water—1 ml. dissolves 0.05 ml., forming nitrous and nitric acids—alcohol about five times as much. It is the most stable of the oxides of nitrogen, decomposing slightly at 900°; phosphorus, actively burning, continues to burn in it. Brought into the air, it takes on oxygen, becoming NO_2. This makes it an important catalyst in the chamber process for making sulfuric acid.

It is prepared by treating copper, silver or mercury with nitric acid, sp.gr. 1.2: the gas obtained is not pure but contains nitrous oxide. The pure gas may be prepared by heating its solution in ferrous sulfate.

Qualitative Detection.—Absorb in water and test for nitrites.

Quantitative Determination.—Absorb in ferrous sulfate 1 : 2: slightly acidified with sulfuric acid: or it can be passed into acidulated permanganate like nitrogen tetroxide. The burning with hydrogen in a platinum capillary is not satisfactory.

Group VII—Unabsorbable Gases. Hydrogen, Methane, Ethylene, Acetylene, Nitrous Oxide, Nitrogen, Carbon Oxysulfide, and the Noble Gases.

Hydrogen was prepared in the sixteenth century by Paracelsus by the usual method of the displacement from acids by metals. Cavendish about 200 years later, in 1766, investigated it thoroughly and gave it the name of "inflammable air." It occurs in volcanic emanations and in the sun. It is produced in the decomposition of organic bodies particularly when oxygen is absent. Hydrogen is the lightest substance, having a sp.gr. of 0.07, the liquid at its boiling point −252.5° having a like density. It is one of the least soluble gases: 100 ml. of water at 20° dissolve about 2 ml., alcohol dissolves about 3 times as much. It is absorbed by some of the metals, hot iron taking up 19 volumes, powdered platinum 50, and palladium black about 900 volumes: cocoanut charcoal absorbs 4.4 volumes. Hydrogen is sometimes said to be spontaneously inflammable, many cases being known of the gas igniting when issuing from cylinders; this has been shown by Nusselt [108] to be due to the dust it contains: the dust,

[107] Ind. Eng. Chem., **14,** 304 (1922); also **17,** 555 (1925).
[108] Zeit. Ver. deut. Ing., **66,** 203 (1922); C. A., **16,** 1640 (1922).

iron rust, etc., issues with the hydrogen with such velocity through the jet as to cause electric sparks, which ignite the hydrogen as it comes in contact with the air. Pails of water and wet rags are used to extinguish the flames from the joints in the balloon filling pipes in the Zeppelin hangar on Lake Constance. The explosive limits with air are from 4.1 to 75%; if the oxygen content be 5% it is also explosive.

Qualitative Detection.—In the absence of olefines (C_2H_4, etc.) and carbon monoxide, by the evolution of hydrochloric acid when hydrogen is passed over cold solid palladium chloride.[109]

Quantitative Determination.—If there be no other combustible gases present, several methods are available:

(*a*) Combustion with a hot platinum spiral in the apparatus of Dennis and Hopkins.[110]

(*b*) Combustion with copper oxide at a temperature of 250°–300° according to Jaeger [111] or in any other similar apparatus.

(*c*) Explosion with oxygen, the converse of the determination of oxygen in air.

Where combustible gases are present the procedure of Campbell and Hart [112] using a 1% solution of palladous chloride at 50°: when fresh, 125 ml. will absorb 25–50 ml. of hydrogen in 90 minutes. Carbon monoxide and dioxide, unsaturated hydrocarbons, and oxygen must be absent. The palladium precipitated can be recovered and a fresh solution made therefrom. Platinum black or palladium sponge or asbestos treated with either has not, in the experience of the writer, given satisfactory results.

Hydrogen has of late assumed great industrial importance, in the synthesis of ammonia, the hydrogenation of oils, changing them to fats of any degree of solidity, the hydrogenation or Berginization of coal and petroleum, and preparation of hydrocarbons resembling petroleum products from it, synthetic motor fuels and for balloons: in this latter connection a thousand cubic feet of pure hydrogen will lift 75 pounds, of the commercial gas about 71 pounds. It is also used for cooling synchronous condensers, increasing their capacity 25%.[113]

It is made commercially by the electrolysis of water or brine, by passing over hot iron, the Lane process, by passing water gas over lime at 500°. Hydrogen is also made by passing natural gas and steam over a catalyst at 870°: the CO found is removed by another catalyst.[114] In this connection it should be noted that attempts are occasionally made to decompose steam by the " waste heat of the boiler furnace " and get hydrogen as a fuel, and oxygen as a by-product. Cast iron retorts are set behind the bridge-wall, steam conducted through them and this passes under the grate and up through the coal. There are several difficulties in the way here: first, at the temperature of 1600° no noticeable (not to say considerable) decomposition of steam takes place whereas the melting point of the cast iron retorts is 1500°, or 100° lower; second, when

[109] Phillips, Am. Chem. J., **16**, 259 (1894).
[110] J. Am. Chem. Soc., **21**, 398 (1899).
[111] J. Gasbeleuchtung, **41**, 764.
[112] Am. Chem. J., **18**, 294 (1896).
[113] Power, **68**, 995. Science, **72**, X (1930). Power, **72**, 902 (1930). Easley, Power, **80**, 362 (1936).
[114] Byrne, Gohr and Haslam, Ind. Eng. Chem., **24**, 1129 (1932).

the mixture of hydrogen and oxygen (supposing it to have been formed) is conducted from the retort, if the temperature drops below 1600° they recombine making steam; third, if it were possible there would be no gain, the heat evolved by the combustion of the gases (if formed) having been previously abstracted from the system to produce any decomposition. A puzzling feature was the fact that when the apparatus was first operated hydrogen was evolved. This was of course due to the decomposition of the steam by the red hot iron $3Fe+4H_2O=4H_2+Fe_3O_4$, and was overlooked.

Another alleged source of gain is that obtained in the so-called " water gas process " of burning coal: Steam is used to produce draft and so cut down smoke, and of course it is decomposed yielding, with the coal, hydrogen and carbon monoxide.

Attention is called to the fact that these are excellent fuels ready-formed " made by waste heat," and the fact lost sight of that the reaction by which they were produced abstracted heat, or cooled the furnace down, and that actually there is no gain in the process. The thermal efficiency of hydrogen engines is very high (45–50%); they use about 21.2 cu. ft. per horsepower hour.[115]

Methane, CH_4, noted by Pliny, forms the fire damp of the coal mines and some part of the fuel for the holy fires of the fire worshippers: when marshy pools are stirred, the gas evolved is largely methane, and it is the chief constituent of natural gas. It too is formed by the decomposition of organic matter by bacteria, septic tank gas being rich in methane. Volta in 1776 observed that it required twice as much oxygen for its combustion as did hydrogen, Berthollet showed it contained hydrogen and carbon, but Henry in 1805 determined its composition.

It has been made from its elements; a common method of preparation is by heating an acetate with an hydroxide, $CH_3COONa+HONa=CH_4+Na_2CO_3$; this does not always furnish pure methane. Another method is by the action of a zinc-copper couple on methyl iodide and alcohol;[116] care must be taken to wash and chill out the iodide vapors. Another method of preparation is by the action of water upon aluminum carbide, $Al_4C_3+12H_2O=4Al(OH)_3+3CH_4$.

Methane is a colorless, odorless gas, about half as heavy as air (sp.gr. 0.55), very slightly soluble in water, 1 ml. dissolving 0.035 ml., and being about 10 times as soluble in alcohol. It burns with a slightly luminous flame of about 5-candlepower (burned at the rate of 5 cubic feet per hour). The explosive limits with air are from 4.9–15.4%. Its boiling point is −164°. Cylinders of the compressed gas are under about 1800 pounds pressure. It is a very stable compound both as regards chemical reagents and heat.

Quantitative Determination.—Methane may be determined by explosion with oxygen or air, as is hydrogen, the procedure being given on p. 2356. Dennis [117] states that while the determination of hydrogen by the Jaeger copper oxide method is very satisfactory, the determination of methane in the same tube at a higher temperature cannot be recommended on account of the time necessary for the oxidation of the methane. He recommends therefore combustion in the Dennis combustion pipette or grisoumeter.

Ethylene or Ethene, C_2H_4, was discovered by Becher and studied by four Dutch chemists in 1795 who made it by dehydrating alcohol with sulfuric acid:

[115] Power, **77**, 90 (1933).
[116] Gladstone and Tribe, J. Chem. Soc., **45**, 154 (1884).
[117] "Gas Analysis," 1929 edn., p. 163.

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U. S. Fish & Wildlife Service
Seattle, Washington

it gave an oily liquid (ethylene chloride) with chlorine and hence received the name olefiant (oil making) gas. Henry showed how it differed from methane and gave it the name of " the heavy hydrocarbon " which still persists, being applied to that portion of coal gas absorbed by bromine or fuming sulfuric acid and also known as " illuminants."

Ethylene is a colorless gas, of peculiar ethereal odor, slightly lighter than air and soluble in 4 times its volume of water at 20°: alcohol dissolves about 10 times as much. Liquid ethylene is found in commerce in cylinders under a pressure of 620 lbs. (42 atmospheres), and the boiling point is −104.3°. It is readily inflammable, giving a flame of about 70 candlepower (burned at the rate of 5 cubic feet per hour). Mixed with 3 times its volume of oxygen, it is powerfully explosive: the explosive limits with air are from 3.2 to 34%.

The principal source of ethylene at present is the gases from the stills used in the cracking of petroleum. During the great war it was made by passing alcohol over clay heated to 500°–600°. Ethylene is used as an anesthetic, mixed with carbon dioxide as a stimulant; oxygen was formerly used for this purpose instead of carbon dioxide, but gave rise to serious explosions in corpore.[118] It is used in a dilution of 1 part per million to color or " age " fruit; one cubic foot per day introduced into a 5000 cubic foot room produces a beautiful golden color in oranges—without, in some cases however, imparting the flavor that goes with it.[119]

Quantitative Determination.—Ethylene is determined by absorption with fuming sulfuric acid containing about 25% of the trioxide: Worstall [120] states this may appreciably attack the saturated hydrocarbons if the time of absorption be more than 15 minutes. Inasmuch as the vapor tension of sulfuric anhydride is higher than that of water, the gas should be passed into the potash pipette to remove this vapor as well as any sulfur dioxide which may be formed. Bromine water may equally well be employed, followed by treatment with potash. In case of the determination of " illuminants " in coal or water gas, bromine water is almost universally used, as it is more rapid: benzol and its homologues while theoretically unattacked by bromine water are mechanically dissolved.

Acetylene (Ethine), C_2H_2, was discovered and analyzed by Edmund Davy in 1836, who prepared it from the black residue obtained in making potassium from cream tartar and charcoal. Berthelot made a thorough investigation of it in 1859. It is formed by the incomplete combustion of many gases and volatile liquids: it was the first hydrocarbon to be synthesized from its elements, by passing an electric arc between carbon poles in an atmosphere of hydrogen; it may also be made by treating ethylene bromide with alcoholic potash, or as now commercially produced by the action of water upon calcium carbide:[121]

[118] "Boston Herald," Jan. 24, 1931.
[119] C. A., **23**, 218 (1929).
[120] J. Am. Chem. Soc., **21**, 245 (1899).
[121] The early preparation of calcium carbide is interesting: Willson at Spray, N. C., was endeavoring to make metallic calcium by heating a mixture of tar and slaked lime in the electric furnace. Instead of getting a bright beautiful metal, a clinker was obtained, which so disgusted him that he threw it into the river. This treatment was promptly followed by the boiling up of the water, bubbles of gas being evolved, which burned when ignited, with a brilliantly luminous flame. Some of the clinker was sent to E. N. Dickerson, a patent lawyer of New York, with the request to ascertain what it and the evolved gas were. The answer was returned that the clinker was calcium carbide and the gas acetylene. See also Wyatt, Eng. and Min. J., **58**, 556 (1894).

generators in which the carbide is dropped into the water are the preferable form. The yield is about 5 cubic feet to the pound or about 11,000 cubic feet per ton. Acetylene when pure has a pleasant ethereal odor; as ordinarily generated, the odor is unpleasant due to compounds of sulfur and phosphorus: air containing 9% can be breathed without ill effect but this mixture is very explosive; the poisonous properties which it is said to possess are due to the sulfur, phosphorus and arsenic compounds contained in it.[122] It is a trifle lighter than air and dissolves in an equal volume of water at 20°; alcohol dissolves 6 times as much and it is quite insoluble in saturated brine. It is very soluble in acetone (1 ml. at 15° dissolves 23 ml. and expands about 5%) and particularly under pressure at 12 atmospheres (180 lbs.) it holds 300 volumes. It burns in the air with an intensely luminous flame of 240–250 candlepower, at 5 cubic feet per hour: the light approaches daylight the most closely of any gas light.

At a pressure of 903 lbs. (63 atmospheres) and 10° acetylene condenses to a liquid which solidifies at −81°, and which it was hoped could be shipped in cylinders, and thus solve the problem of the lighting of isolated houses, but after serious explosions in Paris and Hartford, this was abandoned: the cause of the explosions could not be determined for lack of witnesses.[123] It may have been due to the fact that acetylene being an endothermic compound (47,700 calories being absorbed when it is formed), this same amount of heat becomes free when it is decomposed and expands the hydrogen left by the decomposition (which is equal in volume to the acetylene originally present) producing a pressure, which, coupled with that already existing in the cylinder, is sufficient to burst it; a shock or the detonation of the acetylide of copper would be sufficient to have initiated the explosion.

The explosive limits of acetylene and air vary, according to different observers, from 2.5 to 73,[124] or 1.5 to 80.5%,[125] with the maximum effect at about 7.8. The ignition temperature is 480°, the temperature of the oxyacetylene flame is said to be the same as the electric arc (over 3000°) and is consequently extensively employed in welding and cutting metals even under water!

Qualitative Test.—The reddish-brown coloration produced by contact with ammoniacal cuprous chloride.

Quantitative Determination.—By absorption in bromine water, or fuming sulfuric acid, and subsequent treatment with caustic potash: when passed through ammoniacal cuprous chloride solution a reddish-brown precipitate of acetylide of copper is precipitated. *This is explosive if allowed to dry.* Consequently it must always be kept moist. The precipitate is filtered off, washed free of copper, and dissolved in hydrochloric acid: in case traces of the copper acetylide remain undissolved, the filter is dried, burned, the ash treated with a few drops of nitric acid to dissolve the copper oxide and added to the acid solution above; the copper is here determined electrolytically or in any con-

[122] Chem. Ind., **20**, 53.

[123] A cylinder of compressed acetylene at about 15 atmospheres (without acetone) was not detonated by the fall of a 500-pound pile driver weight 20 feet, nor by a rifle bullet shot through it: when put upon a wood fire—as in a burning car wreck—it detonated splendidly, and fairly promptly. When liquefied, it is explosive at 560 lb. (38 atmospheres) and exerts, when exploded, a pressure of 40 tons per sq. in. (5500 atmospheres). Wolff, Z. angew. Chem., **11**, 919 (1898).

[124] Burrell and Oberfell, Bur. Mines Tech. Paper, 112.

[125] International Critical Tables.

venient way. The copper in small quantities may be determined colorimetrically.[126]

Acetylene dissolved in acetone, " Prestolite," finds use for illuminating purposes (trucks), cutting and welding metals.[127] The cylinders of mild steel about 1/8 inch thick are filled with discs of compressed asbestos, then with acetone, into which the gas is pumped under a pressure of about 225 lbs. (15 atmospheres). Great care must be taken in handling these cylinders, not to drop them: the writer has read of a case in London and also known of a case in Boston in which fatalities occurred by dropping a small cylinder about a foot upon a concrete floor. In the latter case a flaw in the wall of the cylinder left it but half the usual thickness.

The fact that the action of moisture upon calcium carbide produces acetylene may be utilized to determine water in organic compounds or in other cases.

Acetylene can be purified from arsine or phosphine by passing through bleaching powder solution (Lunge) or chromic acid (Ullmann).[128]

Nitrous Oxide, N_2O, was prepared by Priestley in 1772 by the reduction of nitric oxide, perhaps with moist iron filings. It is at present made by heating ammonium nitrate, $NH_4NO_3 = N_2O + 2H_2O$. It is noteworthy that it is evolved when zinc is treated with very dilute nitric acid.

It is a colorless gas 50% heavier than air, with a pleasant smell and taste: when inhaled, it produces a temporary anesthesia with hysterical effects, giving rise to the name of " laughing gas": at 20° water dissolves 0.7 its volume, alcohol about 4 times as much; it boils at −89.8°. It is a supporter of combustion but not of respiration. Liquid nitrous oxide has a pressure of 820 lbs. (55.4 ats.) at 20° and is still sold by the gallon, cylinders of 100, 150 and 450 gallons (60 cu. ft.) being available (100 gallons weigh 1 lb. 9 oz.). It is used in minor surgical operations and as an anesthetic preliminary to ether or chloroform.

Determination.—By explosion with hydrogen, if the volume of the hydrogen be 2 to 3 times the volume of the nitrous oxide, the combustion is aided by mixing detonating gas ($H_2 + O$) so that there are between 26 and 64 volumes of combustible gas to every 100 volumes of incombustible gases, which are the Bunsen ratios.

It should be tested for chlorine and nitric oxide.[129] It may also have a bad odor of rancid oil from the old petroleum oil used in lubrication of the compressor cylinders, which has passed through the filters.

Nitrogen was recognized as a definite body in 1772 by Rutherford of Edinburgh, who called it " mephitic air"; Priestley in the same year found that the residue after carbon had been burned in air, and the gas thus generated absorbed, would support neither combustion nor life, and amounted to 4/5 of the air originally used. It is prepared by burning the oxygen out of air with phosphorus, or hot copper, and by the fractionation of liquid air. This nitrogen contains about 1% of " the noble gases"; the pure gas is obtained by heating ammonium nitrite solution, $NH_4NO_2 = N_2 + 2H_2O$. The ammonium nitrite

[126] Weaver, Sci. Paper Bur. Stds. No. 267 (1916).

[127] See also Mathy, Petr. World, **32**, 59 (1935). Slottman, Oil and Gas J., **34**, 52 (1936), says it is still the best and cheapest, as it uses the least oxygen.

[128] Berichte, **12**, 32 (1879).

[129] C. A., **18**, 2789 (1924).

solution is best prepared by mixing strong solutions of ammonium chloride and sodium nitrite; the oxidation of ammonia or reduction of nitric oxide also yields the pure gas.

It is a colorless, tasteless and odorless gas, a trifle lighter than air: it is very slightly soluble in water, 1 ml. dissolving at 20° 0.015 ml., and alcohol about 10 times as much: it boils at −195.5° (13° lower than oxygen). It is shipped in the usual 220 cu. ft. cylinder under a pressure of 1800 pounds per square inch. It is a remarkably inert gas, combining directly with but few elements: lithium, magnesium, barium and calcium form the nitrides, which when moistened yield ammonia. Strutt [130] finds that when nitrogen containing a trace of oxygen or other gases is subjected to an electric discharge at low pressure, this modified nitrogen acts upon mercury, phosphorus, acetylene and other organic compounds.

Determination.—Nitrogen is energetically absorbed by metallic calcium heated to redness. Fischer [131] has shown that both nitrogen and oxygen may be absorbed by calcium carbide at a temperature of about 800°. Other gases must of course be absent. Nitrogen can be determined in gases by combustion with hot copper oxide after the procedure for the determination of nitrogen in organic compounds.[132] The tube is swept clear of air by carbon dioxide, the gases burned, the tube again swept out, the carbon dioxide absorbed, and the residual nitrogen measured.

Nitrogen is used industrially in making synthetic ammonia, which may be oxidized to nitric acid. (This discovery prolonged the great war for years.) Bradley and Lovejoy made nitric acid by passing an arcing current through the air using copper terminals: it was not found to be economical. Were not heat absorbed in the combination, which must be supplied from an external source, the atmosphere would be set on fire and wholly consumed.

Carbon oxysulfide, COS, Carbonyl Sulfide, was discovered by Than [133] in 1867. It is probably contained in sulfur waters and illuminating gas. It is made by the action of about 50% sulfuric acid upon potassium or ammonium sulfocyanate, $KCNS+H_2O+2H_2SO_4=COS+KHSO_4+NH_4HSO_4$. It is a colorless gas, odorless, when pure, about twice as heavy as air, readily inflammable and poisonous: 0.8 ml. dissolves in 1 ml. of water at 13.5° in which it slowly decomposes giving H_2S and CO_2. The gas could perhaps be determined by alcoholic potash: 1 part potassium hydroxide in 2 parts water and diluted with an equal volume of alcohol: 1 ml. absorbs 72 ml. COS.

Gases of the Helium Group—the noble gases: Helium, Neon, Argon, Krypton, Xenon (and Niton): sometimes also called "the noble gases," because, like the noble metals, they are unaffected by chemical agents.

Helium, He.—Lockyer in 1868 observed in the spectrum of the sun a line very close to the double sodium line, and as it corresponded to nothing terrestrial, the element producing it received the name helium from the Greek word *elios*, the sun. It has since been found in the air, in mineral waters, rare minerals, and by Cady and McFarland [134] of Kansas, in the natural gas of the

[130] Proc. Royal Society, **85** (1911)–**93** (1917).
[131] Ber., **41**, 2017 (1908).
[132] New, J. Soc. Chem. Ind., **11**, 415 (1892).
[133] Annalen Supp., **5**, 236. Hempel, F. Ang. Chem., **14**, 865.
[134] J. Am. Chem. Soc., **29**, 1523 (1907).

Mid-continent and Gulf regions and also Canada, to the extent of 1.84%. Recently a gas containing about 7% has been discovered. Before the war it cost $1300 per cubic foot, but at present about $7 per thousand cu. ft.:[135] it is obtained from the natural gas by compression and cooling. It is present in air to the extent of 1 part in 250,000, and has been obtained from liquid air by fractionation. It is also evolved from an aqueous solution of radium bromide. It is twice as heavy as hydrogen, much less soluble in water, 1 ml. at 20° dissolving 0.0138 ml.—the most insoluble gas, and boils at about −268.5°. It is detected by the spectrum, the double D_3 line being very characteristic, along with seven others. It is used as balloon filling, for the yellow vacuum signs and for lamp filling. Mixed with 1/5 oxygen it is used on account of its slight solubility in the blood to enable divers to come back to normal pressure.

Neon, Ne (**Neon** the new gas), occurs in the air to the extent of 1–2 parts per 100,000, and also in the gases from certain springs. It is prepared by the distillation of the crude argon from liquid air. It is 10 times as heavy as hydrogen, boils at −245.9° and is distinguished by the brilliant red spectrum. This finds extensive industrial use for signs but the gas leaks out eventually through the seals of the wires in the tubes. The blue signs are a mixture of mercury vapor and neon, the green are the same as the blue using an amber tube.

Argon, A (**Argon** idle).—Lord Rayleigh observed that a liter of atmospheric nitrogen weighed 7 milligrams more than chemical nitrogen, showing heavy gases in the air: Cavendish in 1785 had performed a similar experiment with a like result. Rayleigh and Ramsay repeated the experiment, absorbing oxygen with hot copper, nitrogen with hot magnesium, introducing oxygen, sparking the residue, absorbing the nitrous fumes in alkali, and removing oxygen, the gases being circulated for about a week. About 1% of a gas was obtained, having a density 20 times that of hydrogen and an orange spectrum: it forms no compounds, whence its name. The density of the pure gas is 19.9 and the boiling point −186.1°.

Krypton, Kr (**Krypton** hidden), occurs in the air to the extent of 1 part in 20 million: its boiling point is −151.7°, density 41.5, and gives a yellowish-green spectrum.

Xenon, X (**Xenon** stranger), is the least abundant gas, occurring in the air to the extent of 1 part in 170 million: its boiling point is −106.9°, density 65.3 and gives a blue-green spectrum. These last four gases are obtained by the careful fractionation of liquid air.

Niton, Nt, is the emanation produced when an atom of helium is expelled from an atom of radium.

APPLICATIONS OF GAS ANALYSIS AND INTERPRETATION OF RESULTS

It is only within comparatively recent times that Gas Analysis has assumed great importance. The reasons are that the substances with which it deals are so intangible, the apparatus is complicated and fragile, and until lately, competition has not compelled manufacturers to seek every possible source of loss.

[135] Ind. Eng. Chem., **24**, 1435 (1932).

Some of its applications are to:

I. Chimney and flue gases;
II. Producer and fuel gases;
III. City gas;
IV. Sulfuric acid gases;
V. Mine gases;
VI. Electrolytic gases;
VII. Acetylene;
VIII. Atmospheric air;
IX. Natural gas.

I. Chimney and Flue Gases

Here the object is to keep the carbonic acid (CO_2) as high as possible, and to avoid the formation of carbon monoxide: in large plants every additional per cent of carbonic acid means the saving of tons of coal. Savings of 20 to 33% by the use of gas analysis alone have frequently come to the writer's notice. A satisfactory procedure is to post in the fire-room the percentage of carbonic acid obtained by each stoker, and stimulate a rivalry among the men—a bonus in the pay envelope is also effective. The determinations to be made are:

Analysis of Chimney Gases.—Determination of carbon dioxide, oxygen, carbon monoxide, nitrogen, and in some cases hydrocarbons. For this purpose the Orsat apparatus is widely employed: the hydrocarbons may be determined by the Burrell apparatus. These need not be sought unless the carbon monoxide is more than 1%.

Usually a few determinations of carbonic acid will suffice, but for regular work the installation of some form of registering carbonic acid indicator is advisable.

Carbonic Acid Indicators.[136]—These usually depend upon the principle of collecting 100 ml. of the gas, causing it to pass through a suitable absorber and collecting the residue in a bell which floats to a greater or less height according to the residual volume. The fluctuations of this bell are recorded after the usual manner of self-registering barometers or thermometers: the usual time for this analysis and record is five minutes.

By modifying this apparatus slightly, it can be applied to the determination of any absorbable gas as, for example, sulfurous acid or chlorine. It has been adapted to carbon monoxide absorption, but it is not usual or easy.

Haber [137] employs the refractive index of gases to determine the amount of carbonic acid in chimney gas; it gives results within half of 1%; [138] it has also been applied to other gaseous mixtures. The instrument is called the Interferometer or Gas Refractometer and is made by Zeiss of Jena.[139]

Another method for the determination of carbonic acid makes use of the heat conductivity of the different gases; carbonic acid has but about 60% of the heat conductivity of air. Consequently a wire will be hotter in it than in air, all other conditions being the same. This increase in temperature of the wire increases its electrical resistance, from which the per cent of carbonic acid can be determined. The description would take us beyond the limits of

[136] See Bureau of Mines Bulletin No. 91, "Instruments for Recording Carbon Dioxide in Flue Gases." Also Power, **51**, 784 and 1058.
[137] Z. angew. Chem., **19**, 1418 (1906); ibid., **23**, 1393 (1910).
[138] Mohr, ibid., **25**, 1313 (1912).
[139] Bureau of Mines Technical Paper 185, "Use of the Interferometer in Gas Analysis," 1918.

this volume; according to Palmer and Weaver [140] it is by far the best method for the determination, being accurate, sensitive, easily operated and of moderate cost.

The "Ranarex" recorder,[141] an English instrument, consists of two fans rotating each in its own chamber by the same electric motor: these fans cause discs opposite them to rotate, one in air, and the other in the chimney gas. Different torques are produced, depending upon the density of the gas in which the discs rotate: this difference is transmitted by levers to a pointer which indicates the per cent of carbonic acid.

The Determination of Temperature.—This is done by inserting a thermometer, mounted in a metal tube, on the chimney side of the gas sampling tube. Care should be taken to protect it from radiation to and from the walls of the flue. They resemble those used for determining steam temperatures or for "running" varnish. It should register to 360° and, under certain circumstances, one showing 550° may be desirable. A chemical thermometer with long stem may also be employed; it should never be inserted naked into the flue—as a sudden hot blast may break it—but always in a tube of cotton-seed oil or sea sand.[142] These thermometers should be tested for accuracy by comparison with a standard, in a carefully stirred oil bath. The standard should be kept exclusively for the purpose and be allowed to stay in the bath until cool. Sudden cooling of a thermometer changes the zero point. The standard can be certified by the makers or the United States Bureau of Standards.

Electric pyrometers are also of course available for these measurements. An error of five degrees (5°) in the reading of the thermometer affects the final result by about 20 calories.

In case none of these appliances be at hand, the maximum temperature can be determined by utilizing the melting-points of certain pure salts or metals; as tin 232°, bismuth 270°, cadmium 302°, lead 327°, zinc 419°, cadmium chloride 541°, antimony 630°, etc. These can be suspended in the chimney in small covered cast-iron boxes.

Composition of the Coal.—This is determined by the usual methods of organic combustion and is required only for very accurate work.

Calculation:

a. Heat passing up chimney;
b. Pounds of air per pound of coal.

(*a*) ***Heat Passing up Chimney.***—The accurate calculation resolves itself into finding what volume of gas of the composition determined by analysis would be produced by a kilo of the coal used, the analysis of which is known. The temperature of the escaping chimney gases being also known, and their specific heat, the quantity of heat they carry off can be calculated: this divided by the calorific power of the coal gives the per cent of heat lost in the chimney gases. The calculation is rather long and will be found in detail in the author's book.[143]

[140] Bur. Stds. Tech. Paper 249; also Ind. Eng. Chem., **12**, 359 and 894 (1919).
[141] Grant, Industrial Chemist, **2**, 435 (1926).
[142] With *rounded* grains, not river sand, as it would make scratches.
[143] "Gas and Fuel Analysis for Engineers," Wiley.

The formula of Shields: [144]

$$\text{Per cent heat lost} = \frac{\text{Per cent carbon in coal}}{\text{Heating value of coal}} \times \frac{200 + \text{per cent } CO_2}{\text{Per cent } CO_2 + \text{per cent CO}}$$

$\times$rise in temperature in ° C.$\times 0.2864$,

gives results usually 0.5% low, as no cognizance has been taken of the water vapor.

Another formula [145] in which only the carbon dioxide and its temperature enters was proposed by Bunte and gives close results.

For every per cent of carbonic acid present 43.43 calories per cubic meter of flue gases have been developed $= W$; C = specific heat of the flue gases per cubic meter; then W/C represents the initial temperature (which is never attained) the ratio of which to the actual exit temperature of the flue gases shows the heat lost. If T = this initial temperature and t the rise of temperature of the flue gases, then t/T represents the heat lost in the chimney gases.

The following table gives the data for the calculation for both pure carbon and coal of average value.

If there were 11.5% carbonic acid, the initial temperature T would be 1762°; the rise of temperature in the chimney gases is 250°, the loss is 250/1762 or 14.2%. The accurate calculation gives 14.1.

Per Cent of CO_2 in Chimney Gas	Specific Heat of Chimney Gas	Initial Temperature, W/C, ° C.		
		For Carbon $= T$	For Coal $= T$	Diff. for 0.1% CO_2
1	0.308	141	167	16
2	0.310	280	331	16
3	0.311	419	493	16
4	0.312	557	652	15
5	0.313	694	808	15
6	0.314	830	961	15
7	0.315	962	1112	15
8	0.316	1096	1261	15
9	0.318	1229	1407	14
10	0.319	1360	1550	14
11	0.320	1490	1692	14
12	0.322	1620	1830	14
13	0.323	1750	1968	13
14	0.324	1880	2102	13
15	0.324	2005	2237	13
16	0.325	2130	2366	

Finally, for very rapid work, Bunte's Fig. 368 may be used. The results are within 2% for about 12% of carbonic acid. It is used by noting the point where the diagonal line representing CO_2 cuts the ordinate of temperature—the abscissa corresponding to this point represents the per cent loss.

[144] Power, **30**, 1121 (1909).
[145] J. f. Gasbeleuchtung, **43**, 637 (1900).

The following table shows roughly the excess of air, and per cent of heat lost in the chimney gases, their temperature being 518° F.

Per cent CO_2...	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Vol. air more than theory =1.0.....	9.5	6.3	4.7	3.8	3.2	2.7	2.4	2.1	1.9	1.7	1.6	1.5	1.4	1.3
Per cent loss of heat.....	90	60	45	36	30	26	23	20	18	16	15	14	13	12

If the oxygen be from 1.5% to 2% with the temperature of escaping gases at 400–500° F., the fires are too thick; if it be more than 8% they are too thin.

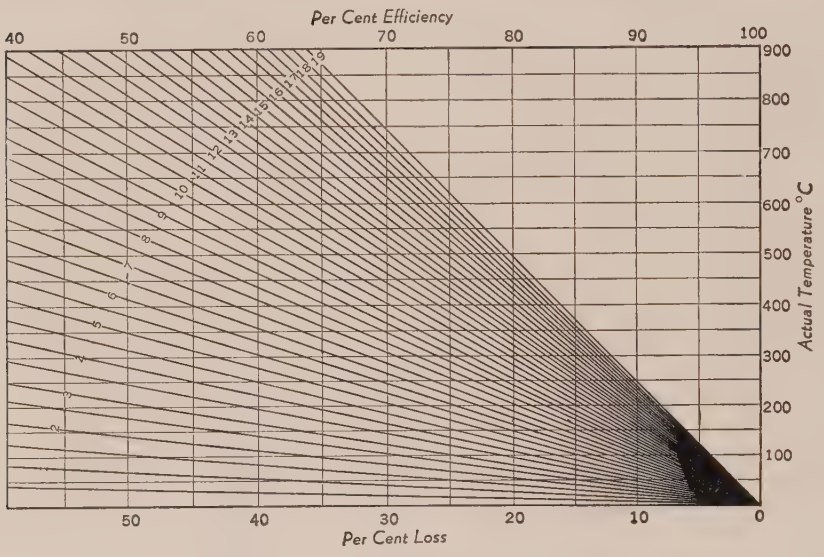


Fig. 368.

(*b*) ***Pounds of Air per Pound of Coal.***—This can be determined by calculating the ratio of carbon to oxygen in the carbonic acid and carbon monoxide and oxygen of the chimney gases, or by the formula of Shields.[146]

$$\textit{Pounds of air per pound of coal} = 2.31\frac{\text{Per cent of carbon in coal}}{\text{Per cent } CO_2 + \text{per cent CO}}.$$

Lockwood [147] has shown how to calculate the excess of air without the use of atomic weights or other constants, from recently developed formulae.

[146] Already cited.
[147] Power, **58**, 461 (1923). J. Soc. Automotive Eng., **12**, 299 (1923).

Theoretical Air per Pound of Combustible.

$$\frac{18.3N_2+34.8CO-69.6O_2}{0.525N_2+5CO+4CO_2-2O_2}. \quad (1)$$

Substitute per cents of N_2, CO_2, etc., as found by the Orsat apparatus.

This formula as well as those including (9) applies to all fuels, solid, liquid and gaseous, except producer and blast furnace gases, where the amounts of nitrogen and sulfur are negligible, and no free hydrogen or combustible but CO is in the flue gas.

Actual Air Used per Pound of Combustible.

$$\frac{18.3N_2}{0.525N_2+5CO+4CO_2-2O_2}. \quad (2)$$

Checking Orsat Gas Analysis.—(*a*) Compare theoretical air weight as obtained by (1) with that calculated from the fuel analysis.

Table A shows the theoretical air required for perfect combustion for different fuels.

Table A

THEORETICAL AIR REQUIRED FOR PERFECT COMBUSTION

Fuel	Vol. Matter %	Theoretical Air per Pound of Combustible
Pure carbon	0	11.6
Gas coke	2.5	11.82
Anthracite coal	6.2	12.22
Semi-bituminous coal	21.0	12.65
Bituminous coal	37.0	12.85
Gasoline (C_6H_{14})	...	15.21

(*b*) Equate the expressions for theoretical air from the gas analysis formula (1) and from the fuel analysis.

$$CO_2+mO_2+nCO=k. \quad (3)$$

Table B shows the different values for these constants for different fuels.

Table B

CONSTANTS TO CHECK ORSAT ANALYSIS

Fuel	*m*	*n*	*k*
Pure carbon	1.00	0.60	20.9
Gas coke	0.98	0.614	20.35
Anthracite coal	0.95	0.63	19.52
Semi-bituminous coal	0.91	0.645	18.7
Bituminous coal	0.88	0.652	18.4
Gasoline	0.70	0.71	14.5

Lockwood gives five other formulae which may be useful, as follows:

$$\textit{Dry gas per pound of combustible} = \frac{22CO_2 + 16O_2 + 14(N_2 + CO)}{0.525N_2 + 5CO + 4CO_2 - 2O_2}. \quad (4)$$

$$\textit{Percentage of excess air} = \left[\frac{69.6O_2 - 34.8CO}{18.3N_2 + 34.8CO - 69.6O_2}\right] \times 100. \quad (5)$$

$$\textit{Water vapor per pound of combustible} = \frac{4.77N_2 - 9CO - 18(CO_2 + O_2)}{0.525N_2 + 5CO + 4CO_2 - 2O_2}. \quad (6)$$

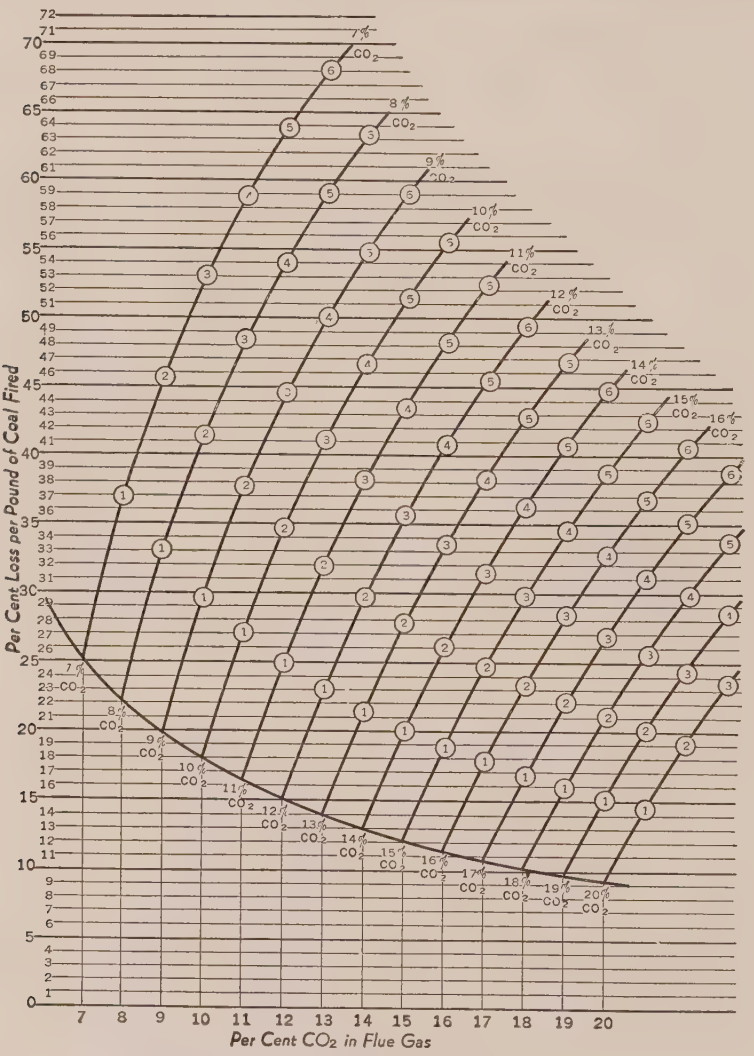


FIG. 369. Brownlie "Combustion," April, 1923.

$$\textit{Percentage of carbon in combustible} = \left[\frac{6(CO_2+CO)}{0.525N_2+5CO+4CO_2-2O_2}\right]\times 100. \quad (7)$$

Percentage of hydrogen in combustible

$$= \left[\frac{0.525N_2-CO-2(CO_2+O_2)}{0.525N_2+5CO+4CO_2-2O_2}\right]\times 100. \quad (8)$$

$$\textit{Ratio of carbon to hydrogen in combustible} = \frac{6(CO_2+CO)}{0.525N_2-CO-2(CO_2+O_2)}. \quad (9)$$

Loss Due to Carbon Monoxide.—For every gram of carbon burned to carbon monoxide there is a loss of 5.66 calories. This is shown graphically in Fig. 369. Tag-Mono Duplex Loss Chart; vertical distances (ordinates) show loss, horizontal distances (abscissae) per cent CO_2 in the chimney gas; the numbers inside the circles the per cent of CO. For example the loss with 14% CO_2 is 13, but if at the same time there be 1% CO, it becomes 20, found by following the curve to the circle with 1 in it. Hence 12% CO_2 with no CO is better than 13% CO_2 with 0.5% of CO.

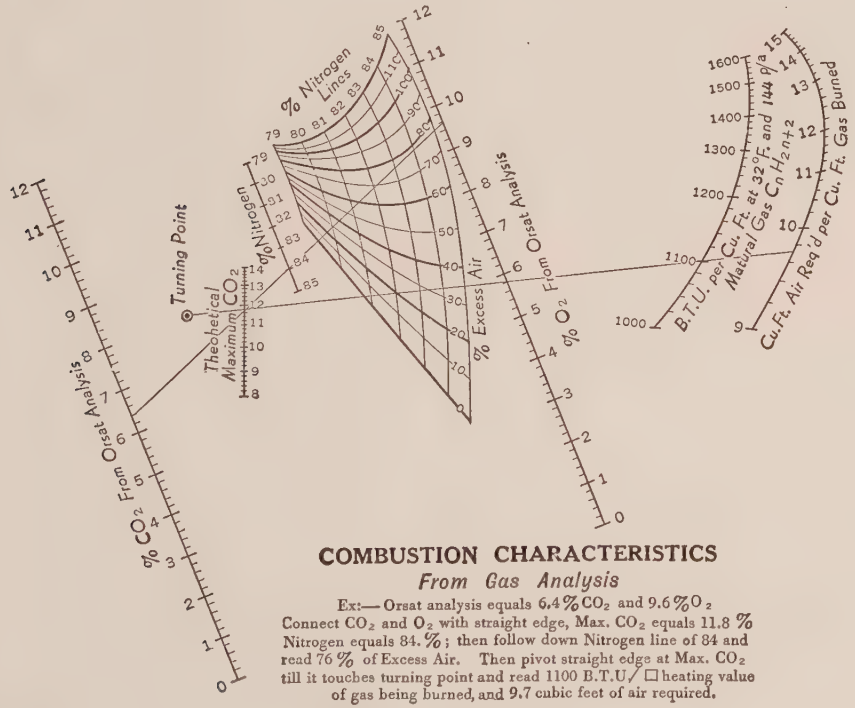

% Nitrogen Lines
Theoretical Maximum CO_2
% Nitrogen
Turning Point
% Excess Air
From Orsat Analysis
% O_2
From Orsat Analysis
% CO_2
B.T.U. per Cu. Ft. at 32°F. and 144 g/a 15
Natural Gas C_nH_{2n+2}
Cu. Ft. Air Req'd per Cu. Ft. Gas Burned
COMBUSTION CHARACTERISTICS
From Gas Analysis
Ex:— Orsat analysis equals 6.4 % CO_2 and 9.6 % O_2
Connect CO_2 and O_2 with straight edge, Max. CO_2 equals 11.8 %
Nitrogen equals 84. %; then follow down Nitrogen line of 84 and
read 76 % of Excess Air. Then pivot straight edge at Max. CO_2
till it touches turning point and read 1100 B.T.U./ ☐ heating value
of gas being burned, and 9.7 cubic feet of air required.

FIG. 370. Marx's Chart.

For gas, Marx's Chart, Fig. 370, is useful.[148] From the Orsat Analysis it shows the maximum CO_2, excess air, the B.t.u. in the gas and the number of cubic feet of air required for combustion.

Smoke.—For the determination of the amount of smoke in the chimney gases, use may be made of the Ringelmann smoke scale. This consists [149] of a series of rectangles ¾ in. × ½ in. filled with cross-hatching lines a greater or less distance apart, with which the density of the smoke can be compared. Or the Eddy smoke recorder may be employed; this consists of a tube of standard length through which the smoke gases are drawn. A standard electric light is fixed at one end of the tube and viewed through the smoke; its density is measured by the extent to which the light is obscured and by a photoelectric cell.

II. Producer and Fuel Gases. Blast-furnace Gas

Here the object is the reverse of that in the chimney gases, to keep the percentage of carbon monoxide as high as possible and, for gas-engine purposes, the per cent of hydrogen constant.

The determinations made are the same as in chimney gas—CO_2, O, CO,[150] N, and oftentimes hydrogen and hydrocarbons; the quantity of *dust* is sometimes important. The heating value is determined as in city gas, p. 2391. The efficiency of conversion would be found by measuring the number of cubic feet of gas made per ton of coal gasified; the calorific power of each (gas and coal) being known, their quotient represents the efficiency. The heat contained in the gas due to its sensible heat, found after the manner of calculating the loss in chimney gases (i.e., volume gas × weight × rise of temperature × specific heat), is to be added to this for accurate work.

As showing *producer gas* practice, the following typical analyses are cited:

	Anthracite [152]	Bituminous [152]	Blue Water Gas [153]	Lignite [153]	Peat [153]	Tan [151, 152]	Wood [152]
CO	27.0	27.0	45.0	22.0	30.6	14.2	13.3
H_2	12.0	12.0	45.0	9.6	6.1	8.7	21.0
CH_4	1.2	2.5	2.0	1.6	5.1	5.6	2.6
C_2H_4	....	0.4	....	0.7	....	....	0.3
CO_2	2.5	2.5	4.0	6.4	5.7	15.0	16.0
N_2	57.0	55.3	2.0	58.9	52.5	56.0	46.7
O_2	0.3	0.3	0.5	0.8	....	0.4	0.1
B.t.u.	137	157	322	....	....	132	140

[148] P. F. Marx, The Refiner and Natural Gas Manufacturer, **10**, 121 (1931).
[149] Power, **40**, 66; also Carter, Power, **74**, 678 (1931).
[150] Tech. Paper 106, Bureau of Mines, "Asphyxiation from Blast Furnace Gas."
[151] With 38.7% H_2O, 3.2% ash.
[152] From "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., 1906.
[153] Richards, J. W., J. Frank. Inst., 415 (1900), quoted from V. Ihering, "Gas Maschinen."

Gas from Different Kinds of Producers

	Down Draft [156]	Up Draft [156]	Suction [154]	Pressure. Taylor [154, 155]	Mond [154]	Blast Furnace [157]	Siemens [157]
CO	17.5	18.3	26.0	22–30	16.0	24	28
H_2	11.8	12.9	18.5	15–7	24.0	2	2
CH_4	1.1	3.1	0.5	3–1.5	2.2	....	....
C_2H_4	.04	0.2	....	....	....	2	2
CO_2	9.2	9.8	8.0	6–1.5	12.4	12	3
N_2	60.1	55.6	47.0	54–60	45.4	60	65
O_2	0.2	.04	....	....	0	....	....
B.t.u.	110	....	145	138	146	106	122

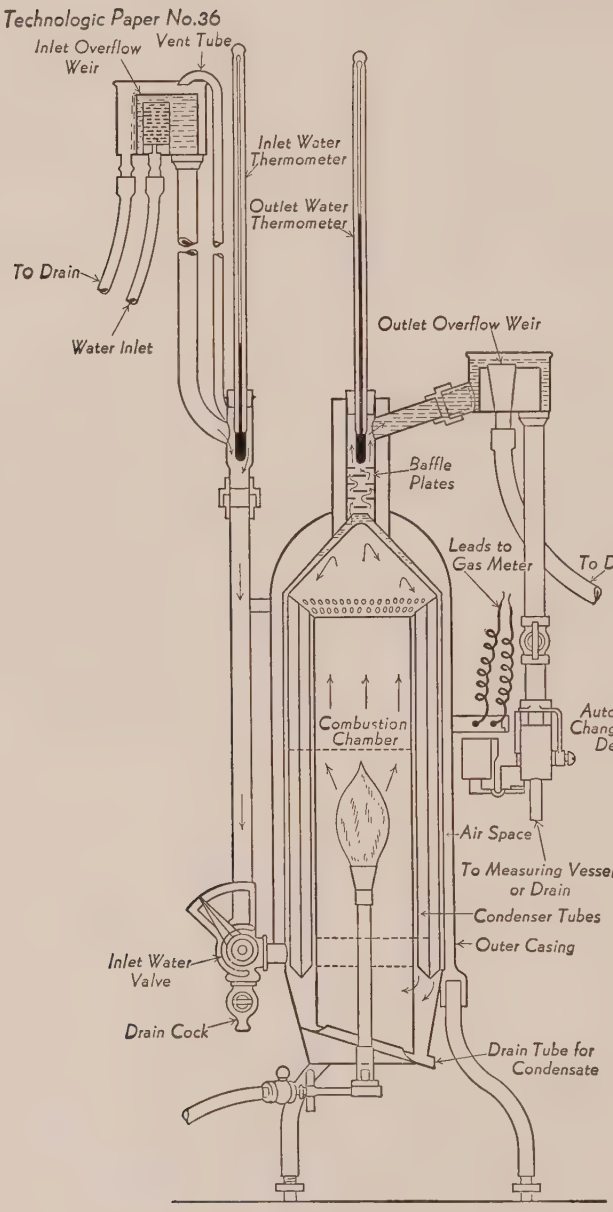
Determination of Dust.—Liddell [158] recommends the following: lump sugar is crushed, and that which is retained by a 90-mesh sieve packed in a 2-in. layer upon copper or brass gauze contained in a glass tube. The sugar is slightly moistened and the gas sucked through it: it is then dissolved in water and the dust collected upon a tared Gooch crucible and weighed. Another procedure and apparatus recommended by the Sargent Steam Meter Co., of Chicago,[159] consists in sucking the gas through a diaphragm consisting of a weighed filter 4½ ins. in diameter, drying and noting the increase in weight. The U. S. Steel Corporation uses the Brady dust filter consisting of a Soxhlet thimble 33×75 mm. in a suitable case, which is inserted in the gas stream. For details of the sampling and procedure which requires careful work, reference may be had to an article by Brady and Touzalin.[160] The dust should not exceed 0.01 grain per cu. ft. at 62° F. and 30 inches. For the methods of cleaning gases see Mark's Handbook, also Prausnitz, **J. Ind. Eng. Ch., 4**, 430 (1932).

III. City Gas [161]

The determinations usually made are as follows:

a. Candle power (rarely done);
b. Calorific power;
c. Sulfur;
d. Ammonia;
e. Analysis;
f. Carbon dioxide;
g. Specific gravity;
h. Tar.

[154] From "Gas Producers and Producer Gas Power Plants," R. D. Wood & Co., 1906.
[155] With anthracite buckwheat.
[156] "Résumé of Producer Gas Investigations," Bureau of Mines Bulletin 13, Fernald and Smith.
[157] Richards, J. W., J. Frank. Inst., 415 (1900), quoted from V. Ihering, "Gas Maschinen."
[158] Power, **38**, 93.
[159] Power, **27**, 331.
[160] J. Ind. Eng. Chem., **3**, 662 (1911).
[161] Circular 48, Bureau of Standards, "Standard Methods of Gas Testing," 1916.



Sargent calorimeter (section)

FIG. 371.

(a) **Candle Power.**—This can be very satisfactorily found using a 60-in. open-bar photometer and Leeson contrast disc. The gas should be burned from a burner commercially obtainable which gives the highest candle power; for gas from 14 to 21 candle power, Sugg's London argand burner, sizes C to F, should be used; for richer gases, Sugg's table top or the Bray slit burner. For a standard of comparison, the sperm candle is convenient, satisfactory, and very extensively used: the Elliott kerosene and Hefner amyl acetate lamps are also employed.

For accurate work the Lummer-Brodhun disc and electric standards, or the Hefner lamp should be used. For the determination of candle power, reference may be had to Circular No. 48 of the Bureau of Standards on "Standard Methods of Gas Testing," 1914, or Stone, "Practical Testing of Gas and Gas Meters."

Carburetted water gas shows from 20–28 candle power, coal gas 14–20, oil gas 45–60, oil-air gas 30–35, gasoline 12–17, acetylene 170–200.

Inasmuch as 75% of the gas now made is used for its heating power (mantle burners), the candle power is infrequently determined.

(b) **Calorific Power.** (*a*) ***Direct Determination.***—This is often determined by the Junkers calorimeter, although others in use are the Sargent, Doherty, and in England the Boys and Simmance-Abady.

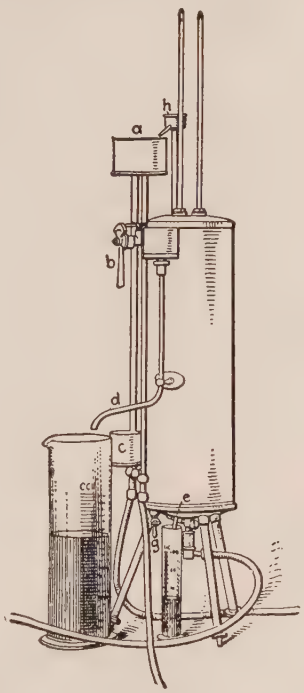


Fig. 372.

The Sargent calorimeter is shown in Fig. 372 and in section in Fig. 371. It consists of a combustion chamber surrounded by a water jacket, this being traversed by a great many tubes. To prevent loss by radiation this water jacket is surrounded by a closed annular air space, in which the air cannot circulate. The whole apparatus is made of copper as thin as is compatible with strength. The water enters the apparatus at the top (water inlet), passes by a thermometer and through the inlet valve, circulates around the apparatus, and passes out by a thermometer to the measuring or weighing vessel: this can be shunted in and out by electrical connections at the meter.

There is not only a very large surface of thin copper between the gases and the water, but the two move in opposite directions, during which process all the heat generated by the flame is transferred to the water, and the waste gases leave the apparatus approximately at atmospheric temperature. The gas to be burned is first passed, to insure constant pressure, through a pressure-regulator and then through a meter, Fig. 373. The source of heat in relation to the unit of heat is thus rendered stationary; and in order to make the absorbing quantity of heat also stationary, two overflows are provided at the calorimeter, making

the head of water and overflow constant. The temperatures of the water entering and leaving the apparatus can be read by the thermometers as shown before; the quantities of heat and water passed through the apparatus are constant. As soon as the flame is lighted, the mercury in the out-going thermometer will rise to a certain point and will remain nearly constant.

Manipulation.—The calorimeter is placed as shown in Fig. 373 so that one operator can simultaneously observe the two thermometers of the entering

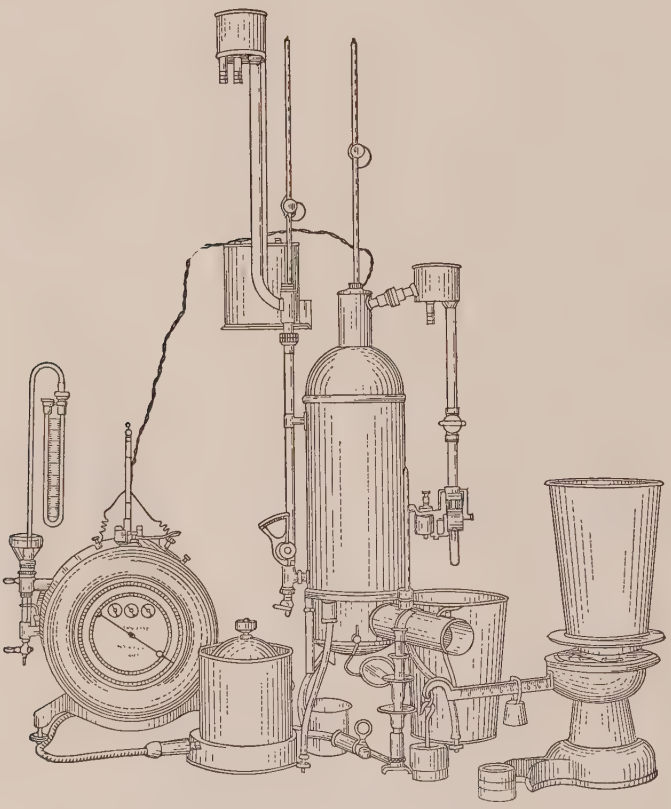


Fig. 373. Hinman-Junkers Calorimeter.

and escaping water, the index of the gas meter, and the measuring or weighing apparatus.

No draft of air must be permitted to strike the exhaust of the spent gas.

The water-supply tube is connected with the nipple in the center of the upper container; the other nipple is provided with a waste tube to carry away the overflow, which latter must be kept running while the readings are taken.

The nipple, through which the heated water leaves the calorimeter, is

connected by a rubber tube with the graduate or a weighed can. The condensed water of the apparatus is caught in a small graduate.

The thermometers being held in position by rubber stoppers and the water turned until it discharges, no water must issue from the drain tube for condensate, Fig. 371, as this would indicate a leak in the calorimeter.

The inlet water valve is now set to allow about two liters of water to pass in a minute and a half, and regulate the gas to flow at the rate of 4 to 7 cu. ft. per hour as may be found to give the highest result with the gas tested. Adjust the air so that the flame shows a slight luminous tip, insert the burner as far as the bracket permits and observe the condition of the flame in the mirror. The excess of air should be as low as possible, and is controlled by the damper in the exhaust port: start with the damper closed, then open slightly, observing the outlet thermometer when this reads at a maximum, i.e., when the greatest heat is given up to the water the damper is in about the correct position.

The flow of water should be regulated so that the temperature of the outgoing water and gas exhaust are the same or differ by no more than 3° C.: the difference between the in-coming and out-going water should be about 10° C. The temperature of the inlet water is noted, the reading of the gas meter taken, and at this same time the outlet tube changed from the funnel to the graduate. Ten successive readings of the out-flowing water are taken while the graduate (2-liter) is being filled and the gas shut off.

A better procedure is to collect about 10 liters of water and weigh it. The thermometer in the outlet can then be read every half minute. For the procedure of the Bureau of Standards, see pp. 2431–2433.

Calculations.—The volume of gas, V, is determined by the difference in the meter readings: this must be reduced to operating conditions, i.e., 60° F., 30 inches and saturated with moisture. The height of the barometric column must be reduced to 0°: this is done by observing its temperature and referring to the proper table in one of the usual "Handbooks of Physical Constants," and noting also whether the scale is brass or glass. The certification correction is also to be applied. The pressure of the gas in inches of water at the meter is changed to inches of mercury (1 in. = 0.07 mm. mercury) and added to the corrected barometric reading; this represents the total gas pressure: its temperature is given by the meter thermometer. Table 9 will then give a means of reducing the volume of gas shown by the meter to operating conditions.

To determine the temperature rise, T, subtract the temperature rise of the inlet water from that of the outlet water: the corrections should have been applied to these thermometer readings and the correction for stem exposure, Table 10.[162] The amount of water, W, heated is determined by weighing, the weights having been verified.

The observed heating value is

$$\frac{W \times T}{V \times F}.$$

F is the reduction factor obtained from Table 9. This heating value is corrected for the effect of atmospheric humidity, Table 11;[163] this is additive to

[162] Bureau of Standards, Circular No. 48.

[163] Circular Dept. Public Utilities of Massachusetts, Gas Inspection Division.

90% humidity. The heating value is further corrected for the loss of heat from the calorimeter which under the usual operating conditions is 1 B.t.u.

Where the water temperature is quite different from room temperature, a correction must be applied, additive if the room is warmer, and subtractive if colder. For calculating total heating value, this correction amounts to 0.5 B.t.u. per degree difference F at a room temperature of 50° F. and increases by 0.1 B.t.u. for each increment of 10° F. room temperature: for calculating the net heating value it is 0.4 B.t.u. for 50°–80° F. room temperature and 0.5 B.t.u. for 90°–100° F. The average of the different runs, which should agree within 1%, corrected for humidity and heat loss, is the *total heating value* of the gas, and is the one to be reported. The *net heating value* is obtained by subtracting the product of the volume of the condensate in ml. $\times$2.3 B.t.u. (0.6° C.) from the observed heating value and correcting for heat loss.

Page 8d from Circular 48, Bureau of Standards, shows how the record is to be kept. (See p. 2433.)

Thomas Recording Meter.—In many gas works this apparatus is in operation and agrees satisfactorily with the Junkers instrument.[164]

Notes.—After setting up the apparatus the *first* thing to be done is to turn on the *water*—(not the gas). Similarly, the *water* should be shut off *last*. All connections and the meter should be tested for leaks before each test. The water level in the meter should be checked daily. Slight drafts caused by moving suddenly near the apparatus will vary outlet readings and vitiate the test. The instrument should not be set up near a window or heating apparatus where radiant heat might affect the readings.

If 0.2 cu. ft. of gas is burned, then an error of 0.1° F. in temperature of water means an error of 4 B.t.u.; an error of 0.01 lb. water, 0.9 B.t.u.; 1° F. in gas temperature, 1.8 B.t.u.; 0.1 in. (barometer), 2 B.t.u.; 1 in. water pressure of gas, 1.5 B.t.u.[165]

The *total* heating value of the gas is the heat given off when the gas is used for heating water or in any operation where the products of combustion pass off below 100° C. The *net heating value* represents the conditions in which by far the greater quantity of gas is consumed, for cooking, heating and gas engines, and is one which should be reported. It should, however, be corrected,[166] to the legal cubic foot, that is, measured at 30 ins. barometric pressure, and 60° F. saturated with moisture.

The chief sources of error are,[167] in adjusting the meter, in measuring the temperature-rise of the water, and in changing over the outflow water to the weighed vessels.

(*b*) ***By Calculation.***[168]—Let us suppose a city gas gave the following analysis: Illuminants 15, carbon monoxide 25.3, methane 25.9, hydrogen 27.9%; the heating value of these gases according to Table 4, page 2426, is as follows:

$$\begin{aligned} 0.15 \times 1900 &= 285.0 \text{ B.t.u.} \\ 0.253 \times 323 &= 81.7 \\ 0.259 \times 1008 &= 261.0 \\ 0.279 \times 325 &= 90.7 \\ \hline & 718.4 \text{ B.t.u.} \end{aligned}$$

[164] Bur. of Standards J. Research, **10**, 99. C. A., **27**, 1239 (1933).

[165] Rept. Joint Committee on Calorimetry, Public Service Commission and Gas Corporations, in the Second Public Service District of New York State, p. 81, 1910.

[166] A difference of 1° C. or of 3 mm. pressure makes a change of 0.3% in the volume. Pfeiffe, J. Gasbeleucht., **50**, 67 (1907).

[167] Technologic Papers of the Bureau of Standards No. 36. "Gas Calorimetry," Waidner and Mueller, page 100, 1914.

[168] U. S. Geol. Survey Paper No. 48; Part III, page 1005.

which is the gross heating value of the dry gas. The correction for the heat lost is found, as with chimney gases, by multiplying the volume of the combustion gases by their weight×specific heat×rise of temperature.

(c) **Sulfur.**—Sulfur, being present in gas in so many forms, is determined by combustion and usually reported in grains of sulfur per hundred cubic feet.

One of the most easily portable and satisfactory forms is that of Hinman and Jenkins described as follows:[169] The upper vessel, Fig. 374, is a " bead glass " 300 mm. long and 60 mm. in diameter; this is filled with large cut-glass beads, held up by a suitable fluted glass, giving a large condensing surface without obstructing the draft. To this bead glass is attached, by a rubber connector, the adapter, 410 mm. long and 50 mm. lower internal diameter. To the upper adapter is attached, by means of the " connecting piece," the lower adapter, 400 mm. long and 40 mm. lower diameter. The connecting piece projects 12 mm. above the top of a rubber stopper, fitting the upper adapter, and is surmounted by a watch-glass deflector carried on platinum wires. An overflow tube carries the condensation to the Erlenmeyer flask hung on the stopper as shown; this tube is so adjusted that some liquid remains on the stopper to keep it cool and to absorb some of the ascending gases. The Bunsen burner is fitted with a lava tip having a 5-mm. hole; surrounding the burner is a glass tube 20 mm. in diameter, forming the inner wall of an annular chamber, of which the outer wall is a glass ring 50 mm. in diameter. Into this chamber, which serves to contain 10% ammonium hydroxide, the lower adapter dips 10 mm.

Fig. 374.

The lower adapter is joined to the " connecting piece " by a short cork-lined metal tube. Although radically different in form, this apparatus is very similar to the Referees' in general principle and in method of use, the principal difference being the use of ammonium hydroxide instead of dry ammonium carbonate as a source of ammonia. About 10 ml. of concentrated ammonium hydroxide is placed in the reservoir about the burner at the beginning of the test and about 5 ml. more added every fifteen or twenty minutes. The gas is consumed at the rate of 0.4 to 0.6 cu. ft. per hour, and 2.5 to 3 ft. burned, if the sulfur is to be estimated gravimetrically; otherwise 1 cu. ft. is enough. When the run is completed the apparatus is allowed to cool and is then flushed four times by pouring 50 ml. portions of water in at the top of the bead tube. To the solutions and washings are added 2–3 ml. bromine water, and it is evaporated to 30 or 40 ml.; an excess of a hydrochloric acid solution of barium chromate is added to the hot solution, it is gently boiled, an excess of dilute ammonia added, again boiled for a minute, filtered and washed. The ammonium chromate in the filtrate (the chromic acid being equivalent to the sulfuric acid in the original solution) after being boiled in a stout flask, with a Bunsen valve, to expel the air, is cooled and titrated directly with stannous chloride (3.25 grams Sn per liter) using starch and potassium iodide to accentuate the end-point.

[169] Jenkins, J. Am. Chem. Soc., **28**, 543 (1906); also Technologic Paper No. 20, Bureau of Standards, McBride and Weaver, "Determination of Sulfur in Illuminating Gas," 1913, also Stone, book cited.

The equations are:

$$(NH_4)_2SO_4 + BaCrO_4 = BaSO_4 + (NH_4)_2CrO_4,$$

$$2(NH_4)_2CrO_4 + 2HCl = (NH_4)_2Cr_2O_7 + 2NH_4Cl + H_2O,$$

$$3SnCl_2 + (NH_4)_2Cr_2O_7 + 14HCl = 3SnCl_4 + 2NH_4Cl + 2CrCl_3 + 7H_2O.$$

The strength of the stannous chloride should be determined at the same time by standard bichromate of potassium.

Or the sulfuric acid can be determined with the turbidimeter as for sulfur in coal. The amount of sulfur is usually from 20 to 30 grains per 100 cu. ft.

Hydrogen Sulfide.[170]—The test is made by hanging a strip of paper moistened with lead acetate solution (1:20) in a bell-jar or tube through which the gas is passing at about 5 cu. ft. per hour and allowing it to act for one minute. Usually several tests are made. The gas should be taken fresh from the main and care should be taken not to confound any black tarry spots with lead sulfide. A properly purified gas should give no test.

It is quantitatively determined by drawing a known volume of the gas through standard iodine solution. Tutweiler [171] measures the gas in a modified Bunte burette over starch solution, runs in a known quantity of standard iodine solution until it is in slight excess. If 100 ml. of gas were taken, the number of milliliters of solution gives the grains of H_2S per 100 cu. ft., 1 ml. iodine $= 0.0017076$ gram iodine $= 100$ grains H_2S per 100 cu. ft.

(d) **Ammonia.**[172]—This is determined by absorption in standard acid colored with cochineal: 10 ml. of HCl [173] are placed in the bulb, Fig. 361, 2–3 drops cochineal solution added, and the gas allowed to bubble through it until the yellow color changes to a deep purple; the meter is now read. The acid is made by diluting 38.2 ml. N/10 HCl to 1 liter, 10 ml. $= 0.01$ grain of NH_3; the cochineal solution is made by treating 3 grams of the ground insect with 250 ml. 20% alcohol, allowing to stand forty-eight hours and filtering. The bubble tube is inserted in series with the gas supply to the sulfur apparatus, Fig. 374 (*c*), so that both determinations are run at one time: the gas is passed through at the rate of 0.5 to 0.6 cu. ft. per hour. Massachusetts law limits the amount of ammonia to 10 grains per 100 cu. ft.

(e) **Analysis.**—The volumetric analysis is carried out according to p. 2355; either bromine water or fuming sulfuric acid can be used to absorb the "illuminants." Besides ethylene, it may be desirable to determine benzol: this is best done according to Dennis, O'Neill and McCarthy [174] by absorption in an ammoniacal solution of nickel cyanide.

Naphthalene.—This is determined in purified gas by passing it through N/20 picric acid solution. White [175] determines it in raw gas by precipitation of the picrate and subsequent recovery of the naphthalene.

[170] Tech. Paper, No. 41, Bureau of Standards, "Lead Acetate Test for Hydrogen Sulfide in Gas."

[171] J. Am. Chem. Soc., **23**, 173 (1901).

[172] Tech. Paper No. 34, Bureau of Standards, "Determination of Ammonia in Illuminating Gas"; also Tech. Paper No. 48 (1916).

[173] This is used by Jenkins; Sulfuric Acid 1 ml. $= 0.01$ grain of ammonia is recommended in T.P. No. 48.

[174] J. Am. Chem. Soc., **30**, 236 (1908).

[175] Proc. Mich. Gas Association, **83**, 1904 (1905).

(f) **Carbon Dioxide.**—This may be determined by Rudorff's method [176] which consists in titrating about a liter of the gas with standard potassium hydroxide. The arrangement and manipulation of this apparatus will be evident from Fig. 375; the capacity of the Woulff bottle must be known and if

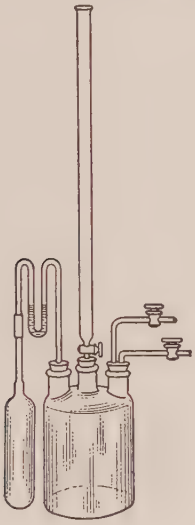


Fig. 375.

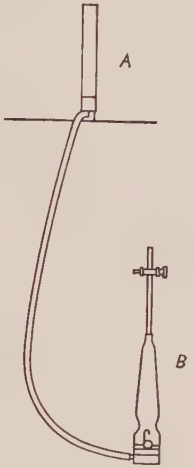


Fig. 376.

the gas contains hydrogen sulfide, it must be absorbed by passage over manganese dioxide. It can also be determined by the usual absorption method.

(g) **Specific Gravity.**[177]—The readiest method depends upon the time of

Composition of Commercial Gases [178]

	CO_2	Ill'ts	O_2	CO	H_2	CH_4	C_2H_6	N_2	Candle Power	B.t.u.
Coal	1.6	4.0	0.4	8.5	49.8	29.5	3.2	3.2	16.1	622
Carb. water	3.0	13.3	0.4	30.4	37.7	10.0	3.2	2.1	22.1	643
Blue water	3.4	0.0	0.9	40.9	50.8	0.2	0.	3.5	....	299
Pintsch	0.2	30.0	0.	0.1	13.2	45.0	9.0	1.6	43.0	1276
Blau	0.	51.9	0.	0.1	2.7	44.1	0.	1.2	48.2	1704
Oil-water	2.6	7.0	0.2	9.2	39.8	34.6	....	6.6	19.7	680
Oil	0.3	31.3	0.	2.4	13.5	46.5	3.9	1.1	38.0	1320
Gasoline	..	1.5	18.5	....	....	C_6H_{14} = 10.3		69.7	16.0	514
Acetylene	..	96.0	0.8	....	....	....	....	3.2	225.0	1350
									H_2S	
Natural	0.3	0.3	0.3	0.5	2.3	92.6	....	3.5	0.2	840–1174
	0.4	....	....	....	....	87.0	9.6	3.0	....	1040

[176] Hempel, op. cit., 262.
[177] See also Chapter II.
[178] Fulweiler, Rogers, "Industrial Chemistry," 5th Ed., 729.

efflux of the gas compared with air; sp.gr. $= \frac{G_2}{A_2}$. G and A represent the times of efflux in seconds of gas and air. The apparatus is that of Schilling and is obtainable from the dealers, or may be constructed according to Jenkins [179, 180] as follows:

" It consists, Fig. 376, of two large rubber stoppers, each having a brass tube, projecting laterally near the large end, and connecting with the hole in the stopper. A glass piece A in the form of a truncated cone fits tightly over one stopper; it is 9 ins. long, 1½ ins. diameter at the base and 1 in. at the top. A similarly shaped piece B 9 ins. long by 1½ ins. diameter at the lower end fits over the second stopper; 2 ins. above the latter the tube has a constriction 1 in. in diameter, and at its upper part is narrowed to a neck 5/16 in. in diameter which is ground on the inside to receive the end of a tube 7½ ins. long and ¼ in. in diameter, in the upper end of which is fitted a platinum plate containing the emission orifice. One and three-fourths inches below this plate is a three-way glass stopcock, and 3 ins. below the latter a scratch surrounds the tube and serves as the upper mark in the escape of the gas.

" Fitted into the hole in the stopper is a hollow cylinder of brass to which is soldered a curved piece of brass wire pointed at the end, which rises 1½ ins. above the surface of the stopper. The two brass tubes projecting from the outside of the stoppers are joined by a piece of rubber tubing 15 to 18 ins. long.

" In using this instrument the larger tube B is filled with water, of the temperature of the room, nearly to the top, the stopcock being turned so that egress of air from the smaller tube is prevented. The larger tube is placed on an elevated surface just high enough so that its bottom is above the level of the scratch on the narrow outlet tube, the cock is turned so that the air may escape through the orifice in the platinum plate, and on the second, when the point of the brass wire breaks the surface of the rising water, a stop watch is started. The latter is stopped when the water exactly reaches the scratch.

" The large tube is lowered, and the stopcock turned so that air may enter through its hollow point. When the water is again all in the large cylinder, the cock is turned to connect the small vessel with the outside air through the platinum tip, the large cylinder is replaced on the elevation and the operation repeated. Results should be obtained which check within one-fifth second.

" Now connect a rubber tube to the gas supply and to the tip of the stopcock, lower the large cylinder and force the water into the latter by means of the gas pressure. Thoroughly saturate the water with the gas to be tested; this may be done by shaking gas and water together and by forcing the water up and down in the small vessel in contact with the gas. Repeat the operation with gas in the same manner as described for air. The calculation is made in accordance with the formula.

" The advantages of this apparatus are its portability, its cheapness, its rapidity and accuracy. When set up, the cylinders are inclined to be a trifle unstable; this may be overcome by fastening a lead plate to the base of each stopper. Four precautions in connection with its use should be emphasized:

[179] Stone, book cited, 261. See also Bureau of Standards, Tech. Papers 89 and 94, by J. S. Edward.

[180] Orton, Geol. of Ohio, VI, 137. See article by Kemp, Collins and Kühn, Ind. Eng. Chem., Anal. Ed. 7, 338 (1935).

(1) The water must be of the room temperature; (2) the water must be thoroughly saturated with the gas; (3) the platinum tip, stopcock, and upper part of the tube must be kept dry and clean; (4) the large cylinder must always, in any one determination, be placed at the same height."

The use of the Edwards Gas Balance has already been explained on p. 2344.

Another method consists in the use of the Lux gas balance. This consists of a balanced globe into which the gas previously filtered through cotton, passes and its specific gravity is read off directly on a scale.

The knowledge of the specific gravity is important, as it is involved in the formula for the calculation of the flow of gas in pipes; it also enables the gas manager to ascertain the weight of gas produced from the coal, and to get an idea of the nature and amount of impurities in the gas, all these being heavier.

(h) **Tar.**—For the estimation of tar, Clemens Winkler [181] recommends the procedure of Tieftrunk: This consists in passing the gas through 25% alcohol and collecting and weighing the tar on a tared filter.

In this country the so-called " Tar Camera " is used: this consists of a brass apparatus [182] into which a 3-inch E and A No. 4970 filter paper is clamped, through which a measured quantity of gas is passed. By the increase of weight of the filter, the amount of tar is determined; the volume of gas may vary from 0.1 to 10 cubic feet.

Stone and Prince [183] use an ordinary Gooch asbestos filter for this purpose. It is weighed after treating with dried and purified gas, subjected to the gas to be tested and dried and weighed as before.

IV. Sulfuric Acid Gases,

the gases involved in the manufacture of sulfuric acid:

a. Burner gases;
b. Nitrogen gases;
c. Oxygen;
d. Gases involved in the contact process.

(a) Burner Gases. Sulfur Dioxide

This gas may be determined by the method of Reich. It consists in aspirating the gas through standard iodine solution (N/10 is suitable) until it is decolorized. The amount of iodine used in the test and the volume of the aspirated gas being known, the percentage of SO_2 can readily be calculated.

$$SO_2+2I+2H_2O=H_2SO_4+2HI$$

Fig. 377 shows a form of apparatus for making this determination. The standard iodine, 5 to 25 ml. N/10 I, diluted to 150 to 200 ml., is placed in the bottle, about 400 ml. capacity, and starch indicator added.[184] The gas to be tested is aspirated through the iodine until the color of the starch blue fades completely. Water which flows out from the graduated cylinder by lowering the aspirating bottle, produces the suction, and the amount measures the

[181] "Die Industrie Gase," page 52; also Hempel, op. cit., 239.
[182] Made by the Steere Engineering Co., Detroit, Mich.
[183] "Gas Age," pp. 531–3, 1920.
[184] Starch indicator may be omitted if the light is good for observing the fading out of the iodine color.

volume of the aspirated gas. From the quantity of iodine used and the volume of the gas required to decolorize the solution the per cent of sulfur dioxide is calculated.

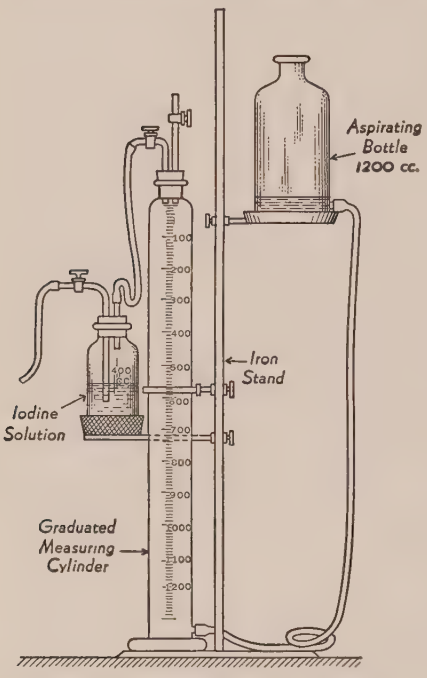


Fig. 377. Portable Reich Apparatus.

Should the contact gas contain SO_3, this is absorbed by passing the gas through 50 to 100 ml. of conc. H_2SO_4, to avoid the action of SO_3 on the rubber tubing of the apparatus. A rapid current of the gas is passed through the acid to saturate it with SO_2 before making the tests.

The Reich method is more applicable for determining small amounts of SO_2. A 12–15-liter graduated aspirating bottle is used in works tests of exit gases for measuring the gas. Since these volumes are not under standard conditions (760 mm. and 0° C.), it will be necessary to convert the volumes obtained in the tests to these conditions, using the formula.

$$V = V^0 \frac{P^0 - w}{760(1+0.00367t)},$$

where V^0 = measured volume, P^0 = observed barometric pressure, t = temperature of the gas, and w = aqueous vapor pressure at temperature of the test.

(b) Nitrogen Oxides

Nitrogen tetroxide, N_2O, and nitrous acid N_2O_3, can best be determined by absorption in standard permanganate (acidulated with sulfuric acid).

Nitric oxide can be determined by passing the gases through soda lye, then by adding air to the collected volume, converting it to nitrogen tetroxide and determining it as above indicated.

Nitrous oxide is determined in the acid-free gases by explosion with hydrogen.

(c) **Oxygen** is usually determined by acid or ammoniacal cuprous chloride—phosphorus is also employed. The percentage of oxygen should not exceed six; a larger amount means that heat is being lost from the chambers by the exhaust gases. Knowing their temperature, the loss of heat can be calculated as with chimney gases.

V. Mine Gases [186]

The gases to be sought are those found in city gas and for most purposes the procedure in p. 2355 can be followed. For small quantities of methane the apparatus of Burrell [187] should be used.

[186] See Technical Paper 14, Bureau of Mines, "Apparatus for Gas Analysis Laboratories at Coal Mines."

[187] Bull. 42, U. S. Bureau of Mines, 17, 42, 1913; also Technical Paper 39, 13; also Bulletin 331.

Table for Reich's Tests for Percentage SO_2, Using Tenth Normal Iodine Solution

Volume % SO_2	25 ml. N/10 Iodine	10 ml. N/10 Iodine	5 ml. N/10 Iodine
12	205 ml. gas	.....	.....
11.5	215 " "	.....	.....
11	226 " "	.....	.....
10.5	238 " "	.....	.....
10	252 " "	.....	.....
9.5	265 " "	.....	.....
9	283 " "	.....	.....
8.5	300 " "	.....	.....
8	321 " "	.....	.....
7.5	344 " "	.....	.....
7	371 " "	148 ml. gas	.....
6.5	402 " "	161 " "	.....
6	438 " "	175 " "	.....
5.5	.....	192 " "	.....
5	.....	212 " "	.....
4.5	.....	237 " "	.....
4	.....	268 " "	.....
3.5	.....	308 " "	154 ml. gas
3	.....	361 " "	181 " "
2.5	.....	436 " "	218 " "
2	.....	.....	274 " "
1.5	.....	.....	367 " "
1.4	.....	.....	393 " "
1.3	.....	.....	424 " "
1.25	.....	.....	442 " "

Sulfur Dioxide in Exit Gases, Pages 1266 to 1269 inclusive.

For determination of *methane* alone, the apparatus of Shaw [188] may be recommended. This determines first the per cent of city gas necessary to make an explosion of definite strength with ordinary air; when this has been done, mine air is used in place of the ordinary air and a smaller percentage of city gas is required—smaller by the amount of combustible gas in the mine air. The strength of the explosion is measured by noting by the ear the force with which the plunger is driven out from the explosion cylinder against a bell.

In case this apparatus be not at hand, Brunck's [189] method can be employed. This consists in burning the methane in a 2-liter Erlenmeyer flask by means of an electrically heated platinum spiral. The flask carrying the spiral in the stopper is sunk inverted in a vessel of water and the current allowed to pass for half an hour, which is sufficient to burn the methane. It is then cooled and 25 ml. BaO_2H_2 (1 ml. = 1 ml. CO_2) added, time allowed for absorption of the carbon dioxide and the excess of BaO_2H_2 determined, and the quantity of methane calculated.

Clowes and Redwood [190, 191] have worked out a method for the detection of inflammable gas in air, employing the " flame cap." When an inflammable atmosphere is brought in contact with a candle or better, a hydrogen flame,

[188] Berichte, **27**, 692 (1894).

[189] O. Brunck, "Die Chem. Unters. d. Grubenwetter," 1908.

[190] "Detection and Estimation of Inflammable Gas and Vapor in the Air," 1896; also Clowes, J. Soc. Arts, **41**, 307. Also McTrusty, "Mine Gases and Gas Testing," 1916.

[191] "Flame Safety Lamps," Bur. Mines Circ. 227, 1924.

the gas burns, forming a " cap," like the colorless flame above the blue cone in a Bunsen burner: the length of the flame is a measure of the percentage of gas, and as little as 0.1% is visible using the hydrogen flame.

The " J. W. Indicator " for the detection of inflammable gases or vapors, depends for its use upon the fact that the resistance of a wire is increased by the heat of combustion of the gas. The gas or vapor is sucked through a tube containing a platinum wire heated to dull redness by a dry-battery current: the burning of the gas increases the resistance of the wire and from this increase the quantity of gas or vapor can be determined.

It is safe, easily portable, easily handled by the ordinarily intelligent and gives direct readings. The Union Carbide Company's indicator is like it in principle, but the heating element was dropped into the tank itself: this was not safe with hydrogen, acetylene or carbon bisulfide. The screens protecting the element necessitated frequent cleansing. Obtainable from the Bullard Davis Co., 67 Wall St., N. Y.

Carbon Monoxide.—Besides combustible gases or " fire damp," it is sometimes necessary to get an idea of the amount of carbon monoxide (" white damp ") in the mine air after an explosion or in the " after damp;" chemical methods, being too slow, use is made of the behavior of birds and mice when exposed to such an atmosphere. To this end they are carried in cages by the rescuing party and their behavior noticed. Canaries show distress in an atmosphere containing 0.15% of CO in five to twelve minutes, or with 0.20% in half this time: Mice are less sensitive,[192] and men may display distress when carbon monoxide is as little as 0.1%, whereas animals may be unaffected. In case either is overcome by the gas, resuscitation can be effected by bringing them out into the open air again. Repeated exposure of the animals to the gas would seem to be without influence.

VI. Electrolytic Gases

Gases from electrolytic chlorine, hydrogen and oxygen generators. The following are to be sought for:

(*a*) Chlorine, (*b*) oxygen, (*c*) carbon dioxide, (*d*) carbon monoxide, (*e*) hydrogen.

(a) **Chlorine.**—Hempel [193] recommends measuring the gas quickly in his burette over water and then sucking in 5 ml. of 50% potassium iodide solution through the capillary and shaking; the diminution in volume gives the chlorine.

The other gases are determined in the usual way. As phosphorus cannot be used for pure oxygen, a specially prepared potassium pyrogallate, is employed; cuprous chloride or ammoniacal cuprous carbonate in the absence of carbon monoxide is very satisfactory.

VII. Acetylene

Commercial acetylene may contain the following gases:

1. Oxygen;
2. Carbon monoxide;
3. Hydrogen;
4. Methane;
5. Nitrogen;
6. Sulfur-containing gases;
7. Phosphine.

[192] Burrell, Seibert and Robertson, Bureau of Mines Technical Paper 62, 1914, "Relative Effects of Carbon Monoxide on Small Animals." Also Tech. Paper 11.

[193] "Gas-Analytische Methoden," 4th Ed., 1913, p. 278.

Oxygen is estimated after the absorption of the acetylene itself in bromine water in the usual way with potassium pyrogallate. Methane and hydrogen would be determined in this residue, after treatment with ammoniacal cuprous chloride to remove the carbon monoxide, by the ordinary explosion methods. Nitrogen would be left as a residue.

Sulfur-containing Gases.—These are most likely organic sulfides, as hydrogen sulfide is probably absent, since the solution from which the acetylene escapes is strongly alkaline. They can be determined by combustion, as in city gas, and best be reported as "total sulfur."

Phosphine is also similarly estimated and the phosphoric acid determined in the usual way: the quantity of PH_3 rarely exceeds 0.05%.

Acetylene can be purified by passing over bleaching powder, through acid cuprous chloride or chromic acid: The candle power is usually given as fifty per cubic foot, or 180–200, when burned at the rate of 5 cu. ft. per hour. The explosive limits are, according to Clowes [194] 3 to 82%, to Burrell and Oberfell, 2.5 to 73%.[195]

VIII. Atmospheric Air

(*a*) Moisture; (*b*) Carbon dioxide; (*c*) Ozone; (*d*) Carbon monoxide; (*e*) Bacteria.

(a) **Moisture** [196] by chemical means. The amount of moisture can be determined by the sling psychrometer, or wet- and dry-bulb thermometer or by the hair hygrometer. The sling psychrometer is the most rapid and accurate —the wet- and dry-bulb thermometers are so arranged that they can be rapidly whirled for fifteen or twenty seconds, stopped and quickly read, the *wet* bulb first; this is repeated until closely agreeing readings are obtained. The humidity is determined in the usual manner from the meteorological tables.

The amount of moisture in the air is probably indirectly responsible for our sensations of comfort or discomfort, rather than the amount of carbon dioxide, as was formerly thought. This moisture controls the heat loss from the body, which loss must be normal—neither too high nor too low. The greater the humidity the less the evaporation, consequently the less the cooling.

For comfort, the higher the temperature the less should be the humidity; the following shows the relation between the two:

Temp., ° F.	60	68 [197]	70	80	90
Relative humidity, %	67	40	49	31	16

(b) **Carbon Dioxide.**—One of the most satisfactory methods is that of Hesse.[198] This consists in absorbing the carbon dioxide from a definite volume of air with standard barium hydroxide and determining its loss of strength.

The air is collected in heavy Erlenmeyer flasks of 100–500 or 1000 ml. capacity, or clear glass bottles; these are stoppered with doubly perforated rubber stoppers carrying glass plugs and the capacity of the flask or bottle noted to the depth of the stopper. A 10-ml. pipette and a 15-ml. glass-stop-

[194] Book cited.
[195] Bureau of Mines Tech. Paper 112, "Explosibility of Acetylene."
[196] Benedict, "The Composition of the Atmosphere with Special Reference to its Oxygen Content," Carnegie Institution of Washington, 1912, Publication No. 166.
[197] For indoor work.
[198] Eulenberg's Vierteljahrschr. f. ger. Med. u. San., N. F., **31**, 2.

pered burette graduated in ml./10 with an 8-cm. tip, complete the outfit; a solution of 1.7 grams of barium hydroxide and chloride (20:1) in a liter of water, *B*, Fig. 378, and of oxalic acid 5.6325 grams per liter (1 ml. = 1 ml. CO_2), with phenolphthalein 1:250, are required. The small bottle attached to the large one is filled with soda lime.

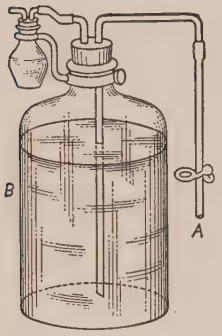


FIG. 378.

The bottles are filled with steam by exposure for three minutes and the vaselined stoppers inserted, or they may be filled with distilled water and opened in the place the air of which is to be examined.

In all this work, it should be remembered that the exhaled breath contains about 400 parts carbon dioxide per 10,000, consequently care should be taken not to contaminate the samples, nor should they be warmed with the hand.

The 10-ml. pipette is partly filled from the tube *A*, Fig. 378, by means of the rubber connector and sucking the liquid into the pipette: it is rinsed, filled and inserted through one of the holes in the rubber stopper of the bottle, the other plug being momentarily opened. The plugs are replaced and the bottles allowed to rest on their sides, with occasional rolling, for twenty minutes. Not more than one-fifth of the solution should be used up by the carbon dioxide present.

During this time, the barium hydroxide should be standardized; to this end a few drops of phenolphthalein and a quantity of the oxalic acid almost sufficient to neutralize the hydroxide should be run into a 100-ml. Erlenmeyer flask from the burette; this should be passed through the doubly perforated stopper; 10 ml. of the barium hydroxide solution are run into the flask as above described, and also the oxalic acid until a pink color appears.

Phenolphthalein is added to the bottles containing the samples, the oxalic acid burette inserted through the stopper and the excess of barium hydroxide titrated.

The barometric pressure and temperature in the laboratory are noted and the volume of the bottle less 10 ml. $Ba(OH)_2$ calculated to standard conditions; the difference in the titer of the barium hydroxide solution gives the volume of carbon dioxide in the bottle; this is calculated into parts per 10,000.

A more rapid method is that of Cohen and Appleyard.[199] This uses a standard solution of lime water colored with phenolphthalein to absorb the carbonic acid: it depends upon the principle that the quantity of air and lime water remaining the same in each case, the rate of its decolorization will vary inversely with the amount of carbon dioxide.

Half-liter bottles are used for the purpose and either filled with water, or a vacuum is produced in them by steaming out and stoppering; the sample is taken by displacing the water or allowing the air to fill the vacuum: 10 ml. of the standard lime water (Reagents) measured with a Vanier overflow pipette run into the bottle, the time noted, the rubber stopper replaced, and the bottle shaken vigorously and continuously, until the pink color disappears when seen over a white paper, and the time again noted. From the time required for decolorization, the amount of carbon dioxide may be found from the table.

[199] Chem. News, **70**, 111 (1894).

Time, Seconds	Parts CO_2 per 10,000	Time, Seconds	Parts CO_2 per 10,000
30	15.6	150	4.4
60	9.9	180	3.8
90	7.2	210	3.6
120	5.5		

Other methods for this determination are more strictly gasometric, measuring the diminution in volume by absorption: Benedict [200] used Sonden's, and Anderson [201] recommends a shortened form of the Pettersson-Palmquist apparatus.

This may be described as an Orsat apparatus using mercury instead of water and with a 25-ml. burette the lower part of which is graduated to 0.0025 ml.; this is connected to a pipette of potassium hydroxide, a delicate manometer and compensating tube. The apparatus is delicate and rapid, but requires a skilled operator to manipulate it. Any form of accurate apparatus may be used.

The amount of carbon dioxide in the outdoor air of the city is about 3.1 parts per 10,000, in the house, 3.7–3.9; with 6–7 parts in a room, the ventilation may be considered as excellent, with 10 parts as about the upper limit. In some theaters which were lighted by gas it approached 50 parts.

(c) **Ozone.**—Probably most conveniently determined by Wurster's method, p. 2370.

Determination of Ozone, Iodide Method of Schönbein.[202] The method depends upon the reaction

$$2KI+O_3+H_2O=I_2+O_2+2KOH.$$

Procedure.—A glass bulb of 300 ml. to 400 ml. capacity (the exact capacity being determined by weighing empty, then full of water) with two tubes at opposite sides, closed by stopcocks, one of which was a three-way cock, is filled with water. The ozone test is introduced into the vessel, displacing the water. The gas is brought to atmospheric pressure by quickly opening and closing one of the cocks. A solution of 2 N potassium iodide is introduced in excess of that required, through the three-way cock by means of a second bulb connected by rubber tube to the vessel after displacing the air in the rubber connection through the cock. The mixture is well shaken and allowed to stand half an hour. The contents of the bulb are washed out with additional iodide solution followed by distilled water and the liberated iodine titrated with standard thiosulfate.

$$1 \text{ ml. N/10 } Na_2S_2O_3=0.0024 \text{ g. } O_3.$$

(d) **Carbon Monoxide.**—The qualitative detection is most certainly effected by the blood test; to this end the gas is drawn through a solution of blood contained in a Wolff, Fig. 361, or similar absorption tube and examined for its

[200] Book cited, also Haldane's.

[201] J. Am. Chem. Soc., **35**, 162 (1913).

[202] Further details of this method may be found in Treadwell and Hall, "Quantitative Analysis."

absorption spectrum. The blood solution is made by mixing ox blood which has been defibrinated by whipping, with an equal quantity of a cold saturated solution of borax; this can be kept (as a side-shelf reagent) in the laboratory for months. This solution is diluted with 19 volumes of water, giving a solution of blood of 1 in 40 which is placed in the absorption tube. The air is drawn through it at a rate of 3 liters per hour, requiring 10 liters in some cases; the solution is put in a thin flat-sided bottle and spectroscopically examined.

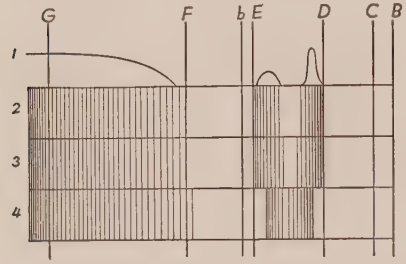


Fig. 379.

Pure diluted blood, Fig. 379, shows two dark absorption bands, spectrum 2, between the D and E line, these are welded into one broad band by reducing agents as NH_4SH, spectrum 4; blood which has absorbed carbon monoxide shows two broader bands in the same place, spectrum 3, which are unaffected by reducing agents.

The quantitative determination depends upon the equation,

$$5CO+I_2O_5=5CO_2+I_2.$$

This has been studied by many, and recently by Vandaveer and Gregg [203] and by the writer. They pass the gas to be tested through two scrubbing Friedrichs (spiral) towers filled with chromic acid at the ordinary temperature, and through solid potassium hydroxide and phosphorus pentoxide. The iodine pentoxide is heated in a U-tube to 150° in an electric air-bath. The highest quality of the reagent should be used, as it is found that even this requires two days' heating at 205°–215° while air or nitrogen is slowly drawn through the apparatus. When not in use, the apparatus should be kept tightly closed, and if the parts of the apparatus be fused together, instead of using rubber connectors, a blank can be obtained in fifteen minutes. Water vapor seems to liberate iodine.

When a blank is obtained, the gas to be tested is passed through the apparatus, and the iodine collected in KI solution, titrated with .001 normal thiosulfate; every 2.27 mg. iodine corresponds to 1 ml. of CO under standard conditions. A complete analysis with an accuracy of 0.002% can be made in about twenty minutes.

Sayers and Yant [204] have worked out a method for the determination of the gas by taking advantage of the carmine red color produced by carbon monoxide blood in tannic acid, and comparing the red produced with standards, as with "Hoolamite," p. 2373.

For the determination of the gas in vehicular tunnels it is absorbed in "Hopcalite," a mixture of the oxides of manganese, copper, cobalt and silver. This produces heat which changes the conductivity of a wire carrying a current; this is converted into per cent carbon monoxide and automatically recorded; the same current also turns on the ventilating fans.[205]

[203] Ind. Eng. Chem., Anal. Ed., 1, 129 (1929).
[204] Tech. Paper 373, Bur. Mines, 1925.
[205] Bur. Mines Tech. Paper 355 1926.

Palladium chloride solution absorbs carbon monoxide with the precipitation of the metal as a black powder: attempts to make in quantitative have not been successful. Other reducing gases must be carefully excluded. See page 2406.

IX. Natural Gas

The determinations to be made are for carbon dioxide, oxygen, methane, ethane, gasoline content and helium.

Burrell and Seibert [206] state that the accurate determination of the constituents of natural gas has proven a stumbling block to gas analysts not familiar with the work. Technical forms of gas-analysis apparatus and established rules for bringing a gas mixture in contact with the absorbents for different constituents are not effective in all cases. Many samples contain absorbable constituents, such as carbon dioxide and oxygen, in extremely small quantities. The fact that oxygen may be a constant constituent of natural gas as it leaves a well has not been determined absolutely. The writers believe that traces of oxygen reported in some samples were due to the contamination of the samples with air. F. C. Phillips [207] detected only minute quantities of oxygen in natural gas from western Pennsylvania after the gas had bubbled continuously for many hours or days through reagents.

Olefin hydrocarbons and carbon monoxide have not been identified in the samples already received at the Bureau of Mines Pittsburgh laboratory. Because of the absorption of higher members of the paraffin series by fuming sulfuric acid and cuprous chloride, a natural gas that does not contain olefin hydrocarbons or carbon monoxide but does contain these higher members of the paraffin series will, when treated with these solutions, undergo a reduction in volume and lead the analyst to a wrong conclusion.

Natural gas as a rule contains a large proportion of paraffin hydrocarbons, in some instances as much as 99%, so that if the paraffins are determined by explosion methods, in which a small quantity (8 or 10 ml.) of gas is used, a slight error of manipulation will be multiplied ten or twelve times in calculating results to a percentage basis. The only hydrocarbon that some natural gases contain is methane; but if a small quantity of sample is taken for the combustion analysis, errors are magnified. The relation between the volume of carbon dioxide and the contraction produced by the combustion may indicate hydrogen, although hydrogen is not present. Though the error in the observed data may be small, yet by the calculation to a percentage basis it may amount to several per cent of hydrogen. Many published analyses of natural gas are undoubtedly much in error owing to such causes.

The paraffin hydrocarbons that are gaseous at ordinary temperatures are methane, ethane, propane, and butane. Since the last two are liquefied [208] at ordinary temperatures by pressures below those found in most producing wells, quantities other than very small proportions carried by the permanent gases would scarcely be found in natural gases coming from wells under much pressure. On the other hand, gases drawn from wells by means of a partial vacuum may contain these and higher paraffins in considerable quantity.

[206] Bull. 42, Bureau Mines, 1913; also 197, 1926.

[207] Phillips, F. C., "Composition of Natural Gas; Researches upon the Phenomena and Chemical Properties of Gases," Am. Chem. Jour., **16**, p. 411 (1894).

[208] Tech. Paper 10, Bureau of Mines.

Determination of Moisture in Gases

The gas to be tested is passed through a dehydrating agent such as phosphorus pentoxide, P_2O_5, alumina, Al_2O_3, or lime CaO, contained in a weighed U-tube, Fig. 380. The following facts should be borne in mind in selecting the dehydrating agent: (*a*) It should not absorb the gas; (*b*) it should not react chemically with the gas. For example—lime or alumina could not be used for determining moisture in sulfur dioxide, nor could phosphorus pentoxide be used in determining moisture in ammonia. For the former, phosphorus pentoxide is best, and for the latter, lime. Alumina that has been carefully heated to 1400° is useful for determining moisture in neutral gases. It should be remembered that gases dried over calcium chloride will give up moisture to strong sulfuric acid, and these in turn will give up moisture to phosphorus pentoxide: Professor Morley has even determined the amount of moisture that is left after this latter treatment.

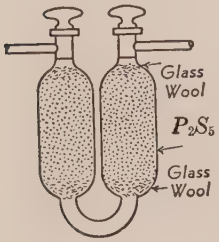


Fig. 380.

Procedure.—The volume of the gases required for the test varies widely according to the percentage of moisture in the gas, 1000 ml. to 10,000 ml. are generally required. For minute amounts of moisture it may be necessary to lead the gas over the dehydrating agent for a given length of time, using a manometer or difference gauge, or a gas meter. The absorption tube is weighed before and after the test and the increase in weight taken as the moisture content of the gas.

Method of Determining Gasoline Vapor in Gaseous Mixtures.[209]—Fig. 381 shows the apparatus for the gasoline-vapor determination. The bulb contains phosphorus pentoxide for removing water vapor. If the latter were not removed it would also be retained at low temperatures and would subsequently exert pressure when measurement was being made of the pressure exerted by the gasoline vapor.

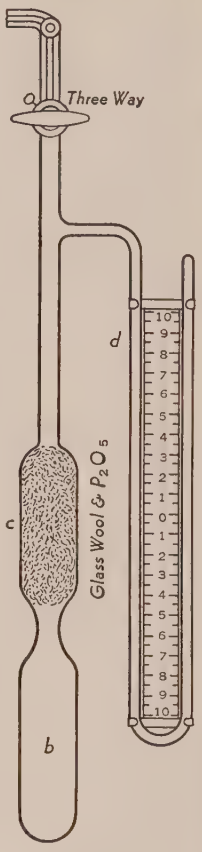


Fig. 381.

To start a determination the apparatus is connected to a vacuum pump and its air exhausted. The mixture of gasoline vapor and air is then introduced at atmospheric pressure, the barometer is read, and the two bulbs are immersed in liquid air contained in a Dewar flask. After about ten minutes, the air is removed from the apparatus with a vacuum pump. The stopcock on the apparatus is then closed, the liquid air in the Dewar flask removed, the gasoline allowed to vaporize, and its pressure read on the mercury manometer attached to the apparatus. The ratio of this pressure to the pressure of the atmosphere gives the percentage of gasoline vapor originally in the air.

[209] U. S. Bureau of Mines, Technical Paper No. 115, Burrell and Boyd.

Method of Sampling

Some samples of gas taken by the bureau's investigators are collected by air displacement in bottles with ground glass stoppers. At the wells or supply pipes a stopper is removed and the gas is allowed to run into a bottle until air has been entirely displaced. Usually a few minutes is sufficient. While the bottle is still in place, the stopper is inserted. As a precaution against leakage, melted paraffin is poured over the stopper. The bottles are then well packed in suitable wooden boxes, and mailed to the bureau's Pittsburgh laboratory. When received at the laboratory the stoppers are removed under mercury and the gas is transferred to and analyzed in an apparatus that contains mercury as the confining fluid. Some samples have been received in strong iron cylinders at the full pressure of the well. Other samples have been collected by a method devised by G. A. Hulett, formerly chief chemist of the bureau, and at present used for collecting some of the bureau's natural gas samples. The method is as follows:

Glass tubes about 17 cm. long and 6 cm. wide are provided at one end with a glass tube extension about 15 cm. long and having a 6 mm. bore. The tube is left open. Natural gas is directed into the sampling tube through the orifice by means of a long slender brass tube. When the air originally in the tube has been displaced, the brass tube is withdrawn and the glass tube orifice closed by placing the finger over it. The sampling tube is then carried to a small alcohol flame and the glass tube extension sealed off.

Simplified Apparatus Used in Analyzing Natural Gas

The apparatus used to analyze natural gas is shown in Fig. 382. The pipette *a* contains potassium hydroxide solution; pipettes *b* and *d* contain alkaline pyrogallate solution. The pipette *c* is the slow combustion pipette. The burette *f* has a capacity of 100 ml. and is graduated to 0.1 ml.

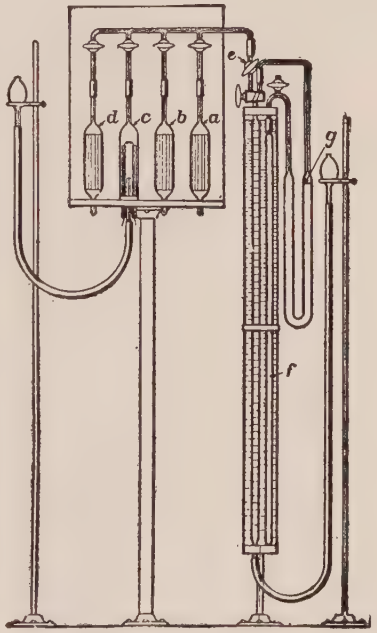


FIG. 382. Laboratory Apparatus for Natural Gas Analysis.

Procedure of Analysis

Natural gas is analyzed at the bureau's Pittsburgh laboratory in the following manner:

Oxygen or other gas left in the horizontal capillary train is displaced by drawing a few ml. of nitrogen from the pipette *d* (Fig. 380) into the burette. This mixture is then allowed to escape into the atmosphere.

About 100 ml. of the gas sample is then drawn by mercury displacement from the sample container into the burette. The sample is measured in the

burette against the pressure existing in the compensating tube *f* by bringing the mercury in the manometer tube exactly to the mark *g*. The sample is then passed successively into the potassium hydroxide and alkaline pyrogallate solutions for the removal of *carbon dioxide* and *oxygen*, burette measurements being made in the same manner as with the original sample.

The residual gas left after the carbon dioxide and oxygen have been determined is discarded and a fresh part of the sample taken for the combustion analysis. The capillary connections are cleared of combustible gas by dilution with air, and about 100 ml. of oxygen is measured into the burette and passed into the combustion pipette. About 35 ml. of the gas sample is then drawn into the burette from the sample container and measured. The platinum wire in the combustion pipette is then heated to a white heat and the gas sample passed at the rate of about 10 ml. per minute into the combustion pipette containing the oxygen. *The paraffins* burn as fast as they enter, so that an explosion consequent upon an accumulation of gas and oxygen can not follow. In analyzing natural gas the authors have obtained the best results by passing the oxygen into the pipette first. When the natural gas is passed in first, the mixture does not always burn as satisfactorily.

After burning, which requires about four or five minutes, the combustion pipette is allowed to cool, and the contraction in volume due to the combustion is measured. The carbon dioxide produced by the combustion is determined by absorption in the potassium hydroxide solution. Finally, the gas is passed into the alkaline pyrogallate solution to make sure that sufficient oxygen has been present for the complete oxidation of the paraffins. Some samples may contain such a large proportion of the higher paraffin hydrocarbons that 100 ml. of oxygen will not be sufficient for the complete oxidation of 35 ml. of natural gas. For such samples a smaller quantity of the gas must be used for the combustion. This statement has especial reference to those natural gases that are used for gasoline manufacture and contain a large percentage of the higher paraffins.

In no case is the burette mercury raised above the upper burette stopcock. The gas remaining in the capillary tubing at any stage of the analysis is brought in contact with the solutions by passing it back and forth several times between the burette and the pipette. After combustion, for instance, some carbon dioxide will remain in the capillary tubing between the combustion pipette and the burette when the gas is drawn back into the burette to record the contraction in volume. After most of the carbon dioxide has been absorbed by the passage of the gas into the potassium hydroxide pipette, the small quantity of carbon dioxide in the capillary tubing is swept out of the tubing into the potassium hydroxide pipette. This operation is repeated in order to insure the complete removal of the carbon dioxide. If this precaution were not taken, an error of considerable magnitude would result.

The apparatus may be used also for the analysis of other industrial gases, such as producer gas and blast furnace gas, when all three of the combustible constituents, carbon monoxide, hydrogen, and methane, can be determined simultaneously by triple combustion.

Calculations from Combustion Data

If the contraction and the volume of carbon dioxide from the combustion of the gas indicate methane, only this constituent is reported. But if the data indicate higher members of the paraffin series, a calculation is made that gives the two predominating constituents. The gaseous hydrocarbons react with oxygen as follows:

$$CH_4+2O_2=CO_2+2H_2O$$
$$C_2H_6+3.5O_2=2CO_2+3H_2O$$
$$C_3H_8+5O_2=3CO_2+4H_2O$$
$$C_4H_{10}+6.5O_2=4CO_2+5H_2O$$

But since the fact that some gases deviate somewhat from the gas laws has been shown by the experiments of Rayleigh, Leduc, Baumé and Perrot, and others, corrections must be made in the case of some gas analyses where this deviation is greater than the experimental error.

The next table gives the theoretical and observed specific gravities of the gases involved in the calculations taken from Landolt and Börnstein.[210]

Below are given the equations for the reactions of methane and ethane with oxygen in which corrections have been made according to the specific gravity determinations shown in this table.

$$0.999\ CH_4+2.000\ O_2=0.994\ CO_2+2H_2O$$
$$0.990\ C_2H_6+3.500\ O_2=1.988\ CO_2+3H_2O$$

Theoretical and Observed Specific Gravities of Certain Gases[211]

Gas	Mol. Wt.	Specific Gravity		Observer	Theoretical
		Theoretical	Observed		Observed
CH_4	16.03	0.5539	0.5544	Baumé & Perrot	0.999
C_2H_6	30.05	1.0381	1.0494	do	.990
C_4H_{10}	58.05	2.0065	2.01	Frankland	.998
CO	28.00	.9673	.96702	Leduc	1.000
CO	28.00	.9673	.96716	Rayleigh	1.000
CO_2	44.00	1.5201	1.52374	Leduc	.994
CO_2	44.00	1.5201	1.52909	Rayleigh	.994
N_2	28.02	.9680	.96737	do	1.001
N_2	28.02	.9680	.96717	Leduc	1.001
O_2	32.00	1.1055	1.10535	Rayleigh	1.000
O_2	32.00	1.1055	1.10523	Leduc	1.000

As the partial pressure of gases in a mixture decreases, the gases more nearly conform in behavior to the gas laws; consequently a table is herein included showing the correct molecular volume to use in the case of carbon dioxide for different partial pressures. The partial pressure of the carbon dioxide has reference to the ratio of the volume occupied by the carbon dioxide

[210] Landolt, H., and Börnstein, R., Physikalisch-chemische Tabellen, 3d ed., 1905, pp. 222–223; Jour. Chem. Phys., 7, p. 367 1909.

[211] At 0° C. and 760 mm. pressure.

found after the combustion to the total volume of residual gas found after the combustion; that is, if the total volume after combustion is found to be 70 ml. and the carbon dioxide is 40 ml., then the partial pressure of the carbon dioxide will be $\frac{40 \times 760}{70} = 434$ mm., and the proper molecular volume, namely, 0.997, will be found from the table.

The foregoing equations have reference to their use at 0° C. and 760 mm. pressure. The following table shows the correct molecular volumes for carbon dioxide at 20° C. and different partial pressures.

Molecular Volume of Carbon Dioxide Corresponding to Different Partial Pressures at 20° C.

Mm. of Mercury	Molecular Vol.
100	0.9993
200	.9986
300	.9980
400	.9972
500	.9965
600	.9958
700	.9951
760	.9950

In compiling this table advantage was taken of the work of Rayleigh,[212] Leduc [212] and Chappius [212] having to do with the determination of the specific gravity and coefficient of expansion of carbon dioxide. The specific gravity determinations were given by Rayleigh and Leduc for carbon dioxide at 0° C. and 760 mm. pressure. Values for 20° C. and 760 mm. pressure were determined from the coefficient of expansion of carbon dioxide between 0° C. and 20° C. A graph was plotted from two values, the deviation from the gas laws at 760 mm. pressure and at 380 mm. pressure.

The coefficient of expansion of ethane between 0° and 20° C. has not been determined, consequently the same molecular volume was used at 20° C., the laboratory working temperature, as was reported by Baumé and Perrot [213] at 0° C. The error resulting from this usage can be disregarded without introducing any appreciable error in the analyses, judging from the molecular volume of carbon dioxide which at 20° C. is only 0.001 different from the value at 0° C.

Below are given the molecular volumes to be used in the case of ethane for different partial pressures.

Molecular Volume of Ethane Corresponding to Different Partial Pressures

Mm. of Mercury	Molecular Vol.
0	1.000
100	.999
200	.997
300	.996
400	.995
500	.993
600	.992
700	.991
760	.990

[212] See Landolt and Börnstein, Phys.-chem. Tabellen, 1912, p. 14.
[213] See Landolt and Börnstein, Physikalisch-chemische Tabellen, 1912, p. 148.

Although the individual paraffins in a mixture of several can not be exactly determined, one will know with a sufficient degree of accuracy which value in the above column to use by accepting the value that corresponds to the percentage of ethane determined from the combustion analysis. It is also true that in natural gas from many places the partial pressure of ethane is so low that only a small deviation from the gas laws occurs. A slight error arises from the probable percentage of propane or butane in a mixture when the combustion analysis indicates only methane and ethane. In most cases the partial pressures of the propane and butane will also be so low that errors in molecular volumes due to their presence can be disregarded.

Methane conforms so closely to the gas laws that no deviation from the given molecular volume need be made for different partial pressures.

The proper equations to use can be determined only from the partial pressures obtained from the analyses. For the purpose of determining the approximate percentage of ethane the theoretical equations can be used.

Application of the Use of Corrected Equations to the Analyses of Natural Gas and Other Gas Mixtures

Although the combustion analysis does not show an accurate distribution of hydrocarbons in a natural gas mixture, it does show the true total paraffin content. The heating value calculated from such an analysis is also correct.

Determinations by the slow combustion method show that the natural gas supplied to Pittsburgh from the Appalachian fields contains about 83% CH_4, 16% C_2H_6, and 1% nitrogen. The proportions vary from time to time during the year.

This gas is almost all methane but contains small amounts of ethane and propane and some of the higher homologues.

A typical analysis with the calculation from the analytical data is given herewith:

Typical Analysis and Calculation

	Burette Readings (ml.)
Sample taken	30.70
Volume after CO_2 absorption	30.70
Portion taken for combustion	30.70
Oxygen added	74.85
Total volume	105.55
Volume after burning	42.30
Contraction	63.25
Volume after CO_2 absorption	7.20
Carbon dioxide	35.10

CH_4 and C_2H_6 are calculated from the theoretical equations as follows:

Let x = methane,
and y = ethane.
Then $2x+2.5y$ = total contraction,
and $x+2.0y$ = CO_2 produced.
$C_2H_6 = 15.1\%$.
$CH_4 = 84.1\%$.

Total paraffins = 99.2%.

They are calculated from the corrected equation as follows:

Let x = methane,
and y = ethane.
Then $2.004x + 2.5y$ = total contraction,
and $0.996x + 2.0y = CO_2$ produced.
$C_2H_6 = 15.7\%$.
$CH_4 = 83.1\%$.

Total paraffins = 98.8%.

Gasoline content is determined according to the method on p. 2408.

Beam Test for Determining the Presence of Suspended Matter in Gases [214]

Tyndall demonstrated that dust particles are responsible for the visibility of rays of light, such as the sun beam or the beam of the searchlight. He did not make clear the best conditions enabling one to see the beam produced by minute amounts of suspended matter in purified gases, nor did he show that a gas free of dust may still produce a beam in presence of liquid mist. The opinion commonly current regarding the conditions necessary to see the beam produced by light rays in purified gas, is that the rays should be parallel and

Beam Test for Suspended Matters in Gases

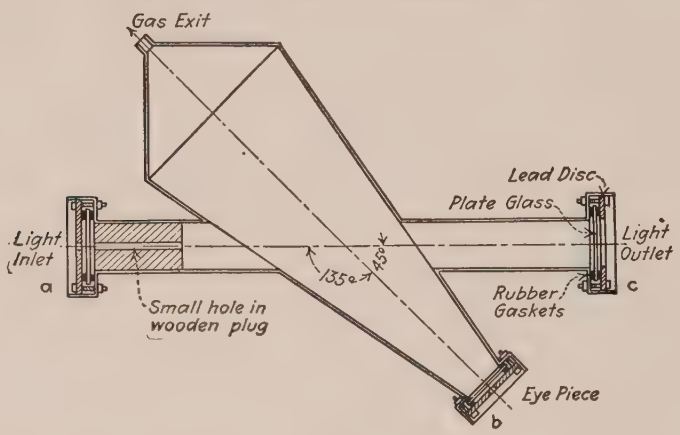


Fig. 383.

should be viewed with the visual axis at right angles to this beam. Observing these conditions the author [214] failed to see the beam using direct sunlight, but discovered that a cone of light from an arc light gave a distinct beam. This led to the discovery that the beam is best viewed by glancing towards the source of light. Accordingly the apparatus shown in Fig. 383 was designed.

For the examination of a corrosive gas, it is advisable to have the chamber of the camera made of a material not affected by that gas. For example, in

[214] Contributed by Wilfred W. Scott.

examining purified contact gas a lead chamber is recommended. The interior of the chamber is blackened with dull paint that is a poor light reflector. In the apparatus shown, circular glass discs close the ends of the tubes "*a*," "*b*" and "*c*." The gas examined enters near the eyepiece "*b*" and passes out at the opposite large end. The ray of light is directed through a small opening, either circular (diam. 1 cm.) or a narrow slit, located at "*a*" and passes through the arm of the tube and out through a glass window at "*c*." The idea is to avoid light reflection in the chamber, as this would cause a glow in the tube and greatly reduce the sensibility of the test.

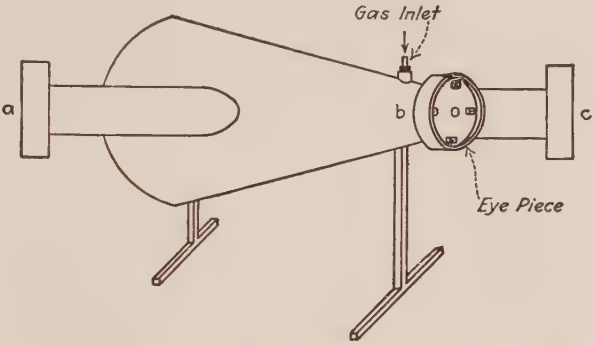


FIG. 384. Apparatus for Ascertaining the Pressure of Suspended Material in a Gas by Means of a Beam of Light.

The beam caused by liquid mist alone appears as a uniform pencil or band of light, whereas dust particles produce a sparkling effect or irregular flashes of light. The beam is more intense with the gas in motion. Within certain limits the intensity of the beam is directly proportional to amount of suspended matter in the gas.

If the gas is dry the beam is completely removed by passing the gas through a three-inch mat of loosely carded purified asbestos. If the gas, thus purified of solid matter, is passed through a liquid the beam again becomes apparent. From this it is evident that the test must be applied to dry gas if it is desired to ascertain the presence of solid matter in suspension.

Fig. 387 shows the apparatus set up for ascertaining the effectiveness of a scrubber in a quantitative determination of the solid and liquid suspended matter in a gas. The apparatus is so arranged that comparisons may be made of the unfiltered gas, by means of a bypass with that of the filtered or purified gas. Advantage is taken of the difference in pressures at *A* and *B*, so that a continuous sample may be taken of the gas without the necessity of an aspirator. A hand arc light shown on the left furnishes the rays of light which enter at "*a*" and pass out into the air at "*c*." The beam is viewed through the eyepiece "*b*." The meter measures the volume of gas aspirated.

DETERMINATION OF SOLID AND LIQUID IMPURITIES IN A GAS[215]

Solid or liquid impurities suspended in a gas may be removed quantitatively by passing the gas through a filter of loosely carded dry asbestos. A filter two

[215] Contributed by Wilfred W. Scott.

inches thick and 1¼ inches in diameter is effective in removing suspended matter completely with gas passing through it at the rate of 2 to 3 liters per second (5 to 7 cubic feet per minute). It is essential that the asbestos be free from condensed moisture as a soggy filter is not effective for gas filtration.

Determination of Sulfuric Acid Mist in Gas.—The gas is aspirated through a filter of well-carded, blue fibre, purified asbestos, the asbestos extracted with water and the extract titrated with standard alkali.

Apparatus.—An ordinary 1¼ inch filter tube funnel (see Fig. 386) with long stem, to permit a sample being drawn directly from the flue may be used. If the gas is supersaturated with moisture it is advisable to use the form of apparatus shown in Fig. 385, the bottle serving as a condensing chamber to avoid water condensation on the asbestos. Occasionally it is necessary to pass the gas through two such chambers to remove the condensed moisture from warm moist gases.

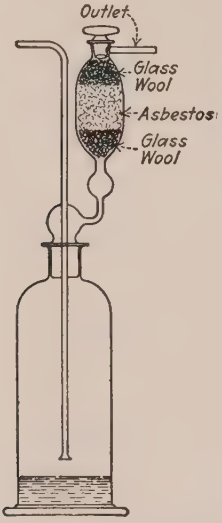


Fig. 385. Apparatus for Determining Solids and Liquid Mist in Wet Gases.

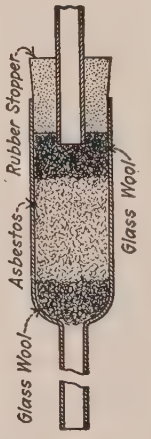


Fig. 386. Filter for Gases.

The funnel is packed first with a layer of glass wool, followed by a two-inch layer of well-carded, purified, blue asbestos, and finally a second layer of glass wool. The glass wool prevents the asbestos plugging the inlet and exit openings. Perforated disks may be used in place of the glass wool.

The asbestos is the blue African form. White asbestos will not give accurate results as this is attacked slightly by dilute sulfuric acid and decidedly so by strong sulfuric. The blue form is not appreciably attacked so that the acid may be extracted as free acid by water. The asbestos is purified by digesting with nitric acid, followed by a second digestion with hydrochloric acid. The material is now thoroughly washed to remove the acids and is dried. The dry asbestos is placed in wide mouth bottles until required. Before using it is

carded or fluffed out by means of a pick and then placed loosely in the funnel to be used in the test.

Impurities in Gases

The Test.—The gas is aspirated through the filter at the rate of about five cubic feet per minute, the gas being measured by a dry gas meter following the apparatus. When a volume of 10 to 100 cubic feet of gas has been aspirated, the amount depending upon the amount of acid mist present in the gas, the asbestos filter is placed in a beaker. (If SO_2 is present in the gas, as is the case in contact sulfur gases, air is first passed through the asbestos to remove the SO_2.) The tube is rinsed out, the rinsings added to the asbestos. The contents of the beaker is now transferred to a two-inch Buechner funnel in position on a half-liter capacity suction bottle. The water is drawn out of the

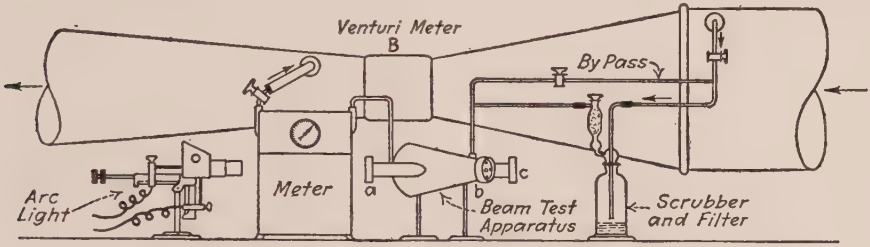


Fig. 387. Apparatus for Determining Solid or Liquid Impurities in Gases.

asbestos and the filtrate passed through the mat, thus formed, to remove the asbestos fibers. The mat is washed with small portions of pure water, until free of acid and the extract, transferred to a beaker, is titrated with standard alkali. N/20 alkali has been found to be satisfactory. Methyl orange is used as an indicator.

Determination of Arsenic in Gas.—The test is the same as the one described for determining sulfuric acid. An aliquot portion of the water extract is taken for a Gutzeit determination of arsenic. The Gutzeit method is described in full in the chapter on arsenic, Volume I. Arsenic in purified contact gas is carried in the acid mist.

Determination of Chlorides.—A portion of the water extract, obtained by the procedure described under the test for acid in gas and filtered through paper if necessary, is examined for chloride by the turbidity test by addition of nitric acid followed by silver nitrate reagent. Comparison is made with a standard using either Nessler tubes or a calorimeter. If the amount of chloride is too great for a turbidity test a gravimetric determination should be made, or the aliquot portion taken should be sufficiently diluted with water to enable the turbidity test to be made. The standard should contain the same amount of sulfuric acid as the sample. The extract should be free of asbestos fiber.

Composition of Asbestos

[2] Asbestos	SiO_2	CaO	MgO	FeO	Al_2G_3	MnO	H_2O
Blue—African	49.0	1.2	2.7	24.4	11.9	—	—
White—Canadian	40.3	—	43.4	.9	2.3	—	13.7
White—Italian	55.9	17.8	20.3	—	4.3	1.1	—

Determination of Nitrogen by the Nitrometer [216]

The nitrometer, Fig. 388, consists of a gas-generating bulb fitted at the top with a two-way cock leading to a dissolving cup and a gas-exit tube, and which has at the bottom a connection for a rubber tube leading to a leveling tube, the whole being filled with mercury to a level just below the upper cock; a cylindrical glass measuring tube graduated from 0–100 ml. connected to a leveling tube

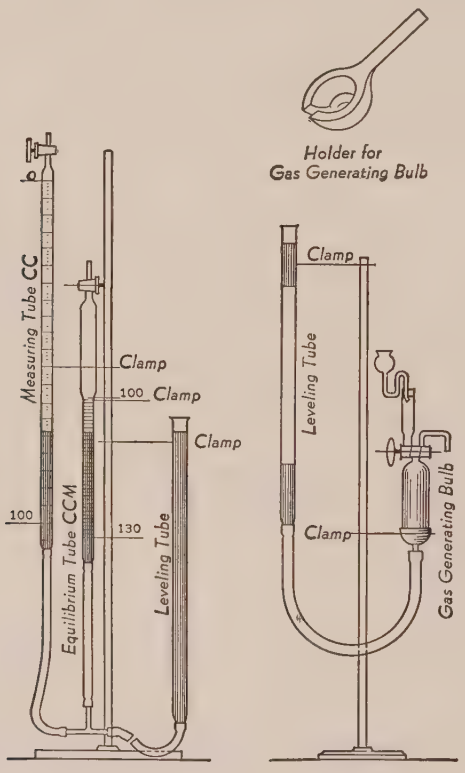


Fig. 388.

through a T-tube leading to an equilibrium tube. The latter is shaped like an inverted 100-ml. pipette graduated downward below the bulb from 100–130 ml. The whole system is filled with mercury so that the measuring tube may be completely discharged by raising the leveling tube.

Adjusting the Equilibrium Tube.—The volume of 100 ml. of dry air at 0° C. and 760 mm. under the temperature and barometric conditions prevailing at the time is calculated, 3 drops of 98% sulfuric acid are drawn into the tube and the level of the mercury fixed in accordance with the calculation. The

[216] Joyce and La Tourette, J. Ind. Eng. Chem., 5, 1017 (1913).

cock of the tube is then closed and sealed with melted paraffin. The volume in this tube may be confirmed at any time by opening the measuring tube and adjusting the leveling tube so that the level is the same in the three tubes. The volume of gas in the equilibrium tube is then read and compared with the calculated volume at the time, a correction in the subsequent gas readings in the measuring tube being made accordingly.

Nitrogen in Potassium Nitrate.—Approximately 0.4 gram potassium nitrate is placed in a weighing tube, dried two hours at 110° C., desiccated twenty-four hours over sulfuric acid and weighed exactly by difference into the cup of the gas-generating bulb. This is dissolved in 9 ml. 95% sulfuric acid, added through a siphon thistle tube, entering the top of the dissolving cup through a tight-fitting rubber stopper. When the salt is dissolved it is drawn into the gas-generating bulb and followed by two washings 1.5 ml. each of 95% acid. The bulb is then shaken with a motion normal to its long dimension until the volume of gas determined by a rough paper scale pasted on the leveling tube becomes constant, this operation taking from three to five minutes.

The gas is passed into the measuring tube, and after standing five minutes the leveling and measuring tubes are so adjusted that the level in the equilibrium tube reads 100 ml. and is the same as the level in the measuring tube. The reading of the latter is then taken. As the temperature and barometric conditions, insofar as they affect the measured volume of the gas, are automatically compensated by the equilibrium tube, and as the gas is washed with sulfuric acid and is, therefore, dry, the percentage of nitrogen may be calculated directly, correcting only for the calibration of the equilibrium and measuring tubes. Seventeen determinations made when the room temperature ranged from 20–28° gave 13.71% nitrogen, the theoretical being 13.84%.

The nitrometer gives reliable results within 0.02% in nitrate nitrogen, using 0.4–0.5 gram sample. It is not available for the determination of nitrogen in celluloid or other substances containing carbon ring compounds which appear to prevent the complete liberation of nitric oxide in the presence of sulfuric acid and mercury.

Besides the corrections for calibration and standardization of the nitrometer in accordance with temperature and barometer, the gas readings should be corrected for solubility of nitric oxide, which diminishes when the temperature goes above 28° C., and the formation of other gases by the breaking up of the cellulose molecule which increases.

The following table gives the algebraic sum of these two corrections for temperatures ranging from 20° to 35° C., for nitrocellulose.

Temp.	Ml.	Temp.	Ml.
20.0–27.5	+0.90	30.0	−0.14
28.0	+0.74	30.5	−0.70
29.0	+0.34	31.0–35.0	−0.94

Compressed Gases and Their Handling [217]

The following gases are available commercially: [218]

Acetylene in acetone (prestolite)	Argon
Ammonia	Helium
Carbon dioxide	Krypton
Chlorine	Neon
Ethylene	Xenon
Hydrogen	Butane, Isobutane
Hydrogen Sulfide	Butylene
Methane	Ethane
Nitrogen	Propane, cyclo-propane
Nitrous oxide	Propylene
Oxygen	Ethyl and methyl chlorides
Sulfur dioxide	Phosgene

They are shipped in cylinders of special steel, of which seven sizes are available, fitted with valves and safety devices, and comply with the regulations of the Interstate Commerce Commission and its Bureau of Explosives. The valve stems used with corrosive gases are of Monel metal (68% nickel, 32% copper) to minimize the gas attack: for ammonia, no copper or copper containing alloy is permissible, as it is attacked energetically. Cylinders containing ammonia and chlorine are made often with siphon valves to enable the liquid gases to be dispensed from them. To prevent the possible mixing of oxygen or nitrous oxide with combustible gases, the cylinders containing these (non combustible) gases are fitted with right-hand threads, whereas the others are fitted with left-hand threads. The table below shows this.

Table Showing the Cylinders for Different Gases

Right-hand Thread	Left-hand
Ammonia	Air
Carbon dioxide	Blau gas
Nitrogen	Chlorine
Nitrous oxide	Hydrocarbons and their chlorides
Oxygen	Hydrogen
Sulfur dioxide	Phosgene
Gases containing oxygen	Combustible gases

When used, these cylinders are usually connected with a gage giving the original pressure, a reducing valve, another gage giving the working pressure, and then a needle valve. Gages showing the rate of flow and the capacity of the different cylinders at different pressures can also be had. Before coupling up this apparatus, the valve on the cylinder itself should always be tried by opening it a little, and then closing quickly, to make sure it does not stick; any foreign matter in the valve will be blown out. Care should be taken to insert suitable washers where necessary. Except with oxygen, a *little* grease, soap or oil may be used on the fittings or washers. *Great care must be used to exclude oil with oxygen fittings*, and new or repaired oxygen gages or fittings must be washed out with carbon tetrachloride until the extract leaves no residue on evaporation: dry air should then be drawn through them until the solvent is evaporated. Failure to do this has resulted in serious trouble. To avoid

[217] Booth, J. Chem. Education, **7**, 1249 (1930).
[218] Circular Ohio Chemical and Mfg. Co., Cleveland.

explosions, a reducing regulator for any other gas must not be used with oxygen or nitrous oxide, and the converse of the statement is equally true. Special fittings to permit the use of apparatus with right-hand threads with left-hand fittings and vice versa had best not be made or acquired, as this fitting has caused fatal accidents.

As has been already stated, cylinders of compressed gases should be handled with care: attention has been called to two fatalities caused by dropping cylinders of compressed acetylene, a distance of about a foot.

APPENDIX

Reagents and Tables

The reagents used in gas analysis, particularly in the absorption apparatus, are comparatively few and easily prepared.

Hydrochloric Acid, sp.gr. 1.10. Dilute "muriatic acid" with an equal volume of water. In addition to its use for preparing cuprous chloride, it finds employment in neutralizing the caustic solutions which are unavoidably more or less spilled during their use.

Fuming Sulfuric Acid.—Saturate "fuming sulfuric acid" with sulfuric anhydride. Ordinary sulfuric acid may be used instead of the other; in this case about an equal weight of sulfuric anhydride will be necessary. *Absorption capacity,* 1 ml. absorbs 8 ml. of ethene (ethylene).

Acid Cuprous Chloride.—The directions given in the various textbooks being troublesome to execute, the following method, which is simpler, has been found to give equally good results: Cover the bottom of a two-liter bottle with a layer of copper oxide or "scale" $\frac{3}{8}$ in. deep, place in the bottle a number of pieces of rather stout copper wire reaching *from top to bottom,* sufficient to make a bundle an inch in diameter, and fill the bottle with common hydrochloric acid of 1.10 sp.gr. The bottle is occasionally shaken, and when the solution is colorless, or nearly so, it is poured into the half-liter reagent bottles, containing copper wire, ready for use. The space left in the stock bottle should be immediately filled with hydrochloric acid (1.10 sp.gr.).

By thus adding acid or copper wire and copper oxide when either is exhausted, a constant supply of this reagent may be kept on hand.

The **absorption capacity** of the reagent per ml. is, according to Winkler, 15 ml. CO; according to Hempel 4 ml. The author's experience with Orsat's apparatus gave 1 ml.

Care should be taken that the copper wire does not become entirely dissolved and that it extend from the top to the bottom of the bottle; furthermore the stopper should be kept thoroughly greased the more effectually to keep out the air, which turns the solution brown and weakens it.

Ammoniacal Cuprous Chloride.—The acid cuprous chloride is treated with ammonia until a faint odor of ammonia is perceptible; copper wire should be kept in it similarly to the acid solution. This alkaline solution has the advantage that it can be used when traces of hydrochloric acid vapors might be harmful to the subsequent determinations, as, for example, in the determination of hydrogen by absorption with palladium. It has the further advantage of not soiling mercury as does the acid reagent.

Absorption capacity, 1 ml. absorbs 1 ml. CO.

Cuprous chloride is at best a poor reagent for the absorption of carbon monoxide; to obtain the greatest accuracy where the reagent has been much used, the gas should be passed into a fresh pipette or cuprous sulfate pipette for final absorption, and the operation continued until two consecutive readings agree exactly.

Acid Cuprous Sulfate.—The chemists of the U. S. Steel Corporation make the solution as follows: The cuprous oxide is prepared in the wet way, as that obtained by the dry method gives a solution that acts too slowly. 100 grams copper acetate are dissolved in a liter of water, filtered if necessary, boiled and reduced with 60 grams of glucose in 400 ml. of water, which is added to the boiling solution. The glucose is prepared by inverting 60 grams of cane sugar in 400 ml. of water with 3 drops sulfuric acid and boiling 5 minutes. The excess acid is neutralized with calcium carbonate, the precipitate allowed to settle and filtered off. When the blue color has somewhat faded, the cuprous oxide is allowed to settle, washed with water by decantation once with alcohol, filtered and dried at 90° to 100° or better in a vacuum desiccator and kept in a tightly stoppered bottle.

Two hundred ml. of c.p. sulfuric acid are diluted with 25 ml. of water in the usual way and cooled, 20 grams of the cuprous oxide are mixed with it in small quantities by grinding in a porcelain mortar until the oxide is in suspension: 25 grams of beta naphthol are gradually added to the mixture in the same manner as the oxide. The mixture is filtered through glass wool kept above 15° to keep the naphthol in solution and well protected from the air. The solution is best fitted for use with the pipette, rather than the burette type of apparatus as the Elliott.

Bromine Water.—Dilute saturated bromine water with twice its volume of water. This then contains about 1% of bromine.

Hydrogen.—A simple and effective hydrogen generator can be made by joining two 6-in. calcium chloride jars by their tubulatures. Pure zinc is filled in as far as the constriction in one, and the mouth closed with a rubber stopper carrying a capillary tube and a pinchcock. The other jar is filled with sulfuric acid 1 : 5 which has been boiled and cooled out of excess of air. The mouth of this jar is closed with a rubber stopper carrying one of the rubber bags used on the simple pipettes.

Standard Lime Water is prepared by adding 6.3 ml. of lime water, saturated at the ordinary temperature with $Ca(OH)_2$, to a liter of distilled water prepared as follows. To a liter of distilled water add 2.5 ml. phenolphthalein (0.7 gm. in 100 ml. 50% alcohol) and titrate this with saturated lime water until a faint pink color is obtained which is permanent for one minute.

Mercury.—The mercury used in gas analysis should be of sufficient purity as not to " drag a tail " when poured out from a clean vessel. It may perhaps be most conveniently cleaned, except from gold and silver, by the method of J. M. Crafts, which consists in drawing a moderate stream of air through the mercury contained in a tube about 3 ft. long and 1¼ ins. internal diameter. The tube is supported in a mercury-tight V-shaped trough, of size sufficient to contain the metal if the tube breaks, one end being about 3 ins. higher than the other. Forty-eight hours' passage of air is sufficient to purify any ordinary amalgam. The mercury may very well be kept in a large separatory funnel under a layer of strong sulfuric acid.

Or Meyer's method [219] may be used. A separatory funnel is used to hold the mercury. The delivery tube of the funnel is slightly narrowed 0.5 cm. from the lower end. Over this side is bound with twine a piece of rather closely woven muslin. The mercury is allowed to flow through the cloth into a solution of mercury nitrate contained in a tall cylinder, with stopcock at the lower end. The tip of the funnel with the muslin dips under the surface of the cleaning solution. The purified mercury is drained off from the bottom of the cylinder. It can also be purified except from traces of zinc by distillation.

Mercury Poisoning.[220]—Very few are aware of the danger to which they are exposed from the vapor of the metal when in ordinary use. This is undoubtedly due to the efficient ventilation of educational laboratories. Air at ordinary room temperature contains when saturated 12 mg. mercury per cubic meter, and 0.01 to 0.001 mg. are found in small closed rooms. This can be detected by a special apparatus using selenium sulfide.[221]

The symptoms of mercurial poisoning are intermittent headache, nervousness, catarrh, weakening of the senses of smell and hearing, inflammation of the eyes, sore spots on the tongue and throat, and reddening and soreness of the gums with toothache. Further symptoms are mental weariness, shown in loss of memory and acumen, and general lassitude and lack of "pep." No medication appears to be of any use, only fresh air and time bring recovery. It seems to act as a cumulative poison, most of the mercury being retained in the lungs.

To avoid poisoning, no spilled mercury should be allowed to lie around in trays, sinks, or on the floor, which should be tight—best covered with linoleum: containers should be stoppered, and work with open mercury done under the hood, unless forced ventilation be employed. It is thought the sufferings of Faraday in later years were due to mercurial poisoning.

Palladous Chloride.—Five grams palladium wire are dissolved in a mixture of 30 ml. hydrochloric and 2 ml. nitric acid, this evaporated just to dryness on a water bath, redissolved in 5 ml. hydrochloric acid and 25 ml. water and warmed until solution is complete. It is diluted to 750 ml. and contains about 1% of palladous chloride. It will absorb about two-thirds of its volume of hydrogen.

Phosphorus.—Use the ordinary white phosphorus cast in sticks of a size suitable to pass through the opening of the tubulated pipette.

Potassium Hydroxide.—(*a*) For carbon dioxide determination, 500 grams of commercial hydroxide are dissolved in 1 liter of water.

Absorption Capacity.—One ml. absorbs 40 ml. CO_2.

(*b*) For the preparation of potassium pyrogallate for special work, 120 grams of the commercial hydroxide are dissolved in 100 ml. of water.

Potassium Pyrogallate.—Except for use with the Orsat or Hempel apparatus, this solution should be prepared only when wanted. The most convenient method is to weigh out 5 grams of the solid acid upon a paper, pour it into a funnel inserted in the reagent bottle, and pour upon it 100 ml. of potassium hydroxide (*a*) or (*b*). The acid dissolves at once, and the solution is ready for use.

[219] J. H. Hildebrand, J. Am. Chem. Soc., **31**, 934 (1909).
[220] Dennis, Ind. Eng. Chem., **18**, 1205 (1926).
[221] Made by the General Electric Co. See Nordlander, Ind. Eng. Chem., **19**, 518 (1927).

If the percentage of oxygen in the mixture does not exceed 28, solution (*a*) may be used;[222] if this amount be exceeded, (*b*) must be employed. Otherwise carbon monoxide may be given off even to the extent of 6%.

Attention is called to the fact that the use of potassium hydroxide purified by alcohol has given rise to erroneous results.

Absorption Capacity.—One ml. absorbs 2 ml. O_2.

Sodium Hydroxide.—Dissolve the commercial hydroxide in three times its weight of water. This may be employed in all cases where solution (*a*) of potassium hydroxide is used. The chief advantage in its use is its cheapness. Sodium pyrogallate is, however, a trifle slower in its action than the corresponding potassium salt.

Table 1 [223]

CONSTANTS OF THE GASES

	Gas	Sp.Gr. to Air Calculated	Wt./Liter in Grams, 0°, 760 mm.	Sp.Ht./Cu.Ft. at Atmos. Press., 62° F., C.P.	Press. at 20° C. in Lbs.	Explosivity % Gas in Air	Sol. of Gas in 1 Liter of Water in ml.		B.Pt. ° C.	M.Pt. ° C.
							At 0°	At 20° C.		
I	NH_3	0.5971	0.7710	.0234	125	16.5 –26.8	1,176,000	702,000	– 33.1	– 77.7
	NO_2	1.5906	2.0563						22	– 9
	Cl_2	2.4494	3.214		97			2,229	– 34.6	–102
	HCl	1.2684	1.6392	.0183	620		505,000	444,000	– 85	–111
	$(CN)_2$	1.7968	2.3229		73			4,500	– 20.5	– 34.4
II	HCN	0.9359	1.2096						26	– 14
	SO_2	2.224	2.9269	.0260	48		79,789	39,374	– 10	– 72.7
	H_2S	1.1769	1.5392		150	4.3 –46.0	4,370	2,905	– 60.2	– 82.9
	SiF_4	3.60	4.684		50		Completely		– 90	– 77
	CO_2	1.5290	1.9777	.0243	870		1,713	874	– 78.5	– 56
	PH_3	1.1829	1.5293				2,500?		– 87.4	–132.5
III	AsH_3	2.695	3.4944				200		– 54.8	–113.5
	SbH_3	4.360	5.6						– 17	– 83
IV	O_2	1.10523	1.4290	.0182	1800		49.61	31.71	–183	–218.4
	O_3	1.624	3.0000						–112	–251
V	CO	.9671	1.2504	.0180		12.5 –75.0	35.37	23.19	–190	–212.6
VI	NO	1.0367	1.3402	.0183			73.81	47.06	–150.2	–160.9
	H_2	.0694	.08985	.0181		4.15–75.0	21.53	18.37	–252.77	–259.2
	CH_4	.5545	.7168	.025		4.9 –15.4	55.63	33.08	–161.4	–184
	C_2H_2	.9056	1.173	.024		1.5 –80.5		103	– 83.6	– 81.8
VII	C_2H_4	.9684	1.2609	.029		3.2 –34.0	226	122	–103.9	–169.4
	N_2O	1.5301	1.977	.0256			130.52	67.00	– 89.7	–102.4
	N_2	.9673	1.2505	.0182			23.59	15.98	–195.8	–209.8
	COS	2.075	2.727				1,348	568	– 48.0	–138
	air	1	1.293	.0241			24.7	17.0		

[222] Clowes, Jour. Soc. Chem. Industry, **15**, 170 (1896).

[223] See also in this connection Bur. Mines Bulletin 279. Coward & Jones, "Limits of Inflammability of Gases and Vapors." Also Bulletin 30, "Explosibility of Methane and Natural Gas."

Table 2

TABLE SHOWING THE TENSION OF AQUEOUS VAPOR AND ALSO THE WEIGHT IN GRAMS CONTAINED IN A CUBIC METER OF AIR WHEN SATURATED FROM 5° TO 30° C.[224]

Temp.	Tension, mm.	Grams	Temp.	Tension, mm.	Grams	Temp.	Tension, mm.	Grams
5	6.5	6.8	14	11.9	12.0	23	20.9	20.4
6	7.0	7.3	15	12.7	12.8	24	22.2	21.5
7	7.5	7.7	16	13.5	13.6	25	23.6	22.9
8	8.0	8.1	17	14.4	14.5	26	25.0	24.2
9	8.5	8.8	18	15.4	15.1	27	26.5	25.6
10	9.1	9.4	19	16.3	16.2	28	28.1	27.0
11	9.8	10.0	20	17.4	17.2	29	29.8	28.6
12	10.4	10.6	21	18.5	18.2	30	31.5	29.2
13	11.1	11.3	22	19.7	19.3			

Table 3

SPECIFIC HEATS B.t.u. PER POUND OF GASES AT CONSTANT PRESSURE c.p.

		Volumetric[225]
Air	0.241	0.019
Carbon dioxide	0.210	0.027
Carbonic oxide	0.243	0.019
Hydrogen	3.420	0.019
"Illuminants"	0.400[226]	0.040
Methane	0.593	0.027
Nitrogen	0.247	0.019
Oxygen	0.217	0.019
Aqueous vapor	0.480	....

The "volumetric" specific heat is the quantity of heat necessary to raise the temperature of 1 cu. ft. of gas from 32° F. to 33° F.

[224] Gases are about 10 times as soluble in kerosene, Z. physik. Chem., **1**, 70 (1887).
[225] H. L. Payne, Jour. Anal. and Applied Chem., **7**, 233.
[226] Ethylene.

Table 4

CALORIFIC POWER OF VARIOUS GASES [227] IN BRITISH THERMAL UNITS PER CUBIC FOOT AT 30 IN. PRESSURE

Name	Symbol	60° F. Initial [231]	32° F. Initial 32° F. Final	Ignition Point ° F.
Hydrogen	H_2	325	345.4	1085 [230]
Carbonic oxide	CO	323	341.2	1200 [230]
Methane	CH_4	1008	1065.0	1230
Illuminants [228]	....	1900 [232]	2000.0	....
Ethane	C_2H_6	1778	1861.0	1140
Propane	C_3H_8	2513	2657.0	1015
Butane	C_4H_{10}	3269	3441.0	....
Pentane	C_5H_{12}	4022	4255.0	....
Hexane [229]	C_6H_{14}	4744	5017.0	1400
Ethylene	C_2H_4	1583	1674.0	1010 [230]
Propylene	C_3H_6	2340	2509.0	940
Benzene	C_6H_6	3741	4012.0	....
Acetylene	C_2H_2	1483	1477.0	788 [230]

Table 5

ENGLISH AND METRIC EQUIVALENTS

1 pound	= 453.59 grams	1 calorie	= 3.969 B.t.u.
1 cubic inch	= 16.39 ml.	1 cubic meter	= 35.31 cu. ft.
1 cubic foot	= 28.315 liters	1 calorie per cu. meter	= 0.1124 B.t.u.
1 B.t.u. per cu. ft.	= 8.89 calorie per cubic meter		
1 in. H_2O pressure	= 1.87 mm. Hg pressure	1 mm. Hg pressure	= 0.535 in. H_2O pressure

[227] H. L. Payne, already cited.
[228] Where obtained by cracking oil.
[229] The chief constituent of gasoline.
[230] Dixon and Coward, Proc. Chem. Soc., **26**, 67.
[231] Gas Chemists' Handbook.
[232] Calculated.

Table 6

The following table assembled from compilations by Henderson and Haggard [233] shows the:

DANGEROUS CONCENTRATIONS OF THE VARIOUS GASES IN PARTS/MILLION

	Ammonia	Arsine	Carbon Monoxide	Chlorine	Hydrochloric Acid	Hydrocyanic Acid	Hydrofluoric Acid	Hydrogen Sulfide	Nitrous Fumes	Phosphine	Sulfur Dioxide	Gasoline Vapors	Benzene, Toluene, Xylene
Least detectible odor....	53			3.5							3–5	300	
Least am't irritating to eyes.....	698										20		
Least am't irritating to throat.....	408			15.1					62		8–12		
Least amount causing coughing.....	1720			30.2					100		20		
Maj. concentration for prolonged exposure...	100		100	1.0	10		3	100–150	39		10		
Maj. concentration for ½–1 hr. exposure.....	300–500		600	4–	50	50–60	10	300		100–200	50–100		
Dangerous for short exposure.....	2500–4500	50	1500–2000	40–60	1000–2500	120–150	50–250	500–700	117–154	400–600	400–500	11,000–22,000	3130–4700
Rapidly fatal for short exposure.....	5000–10,000	30 min. 250	4000	1000		3000		3000	775	2000		24,300	19,000

[233] "Noxious Gases and the Principles of Respiration Influencing their Action."

Table 7

VOLUMETRIC FACTORS

1 ml. of the Different N/10 Solutions Corresponds to the Following Volumes and Weights of the Different Gases

Gas	HCl		$KMnO_4$		$Na_2S_2O_3$		NaOH		$AgNO_3$		I	
	Ml.	Mg.	Ml.	Mg.	Ml.	Mg.	Ml.	Mg.	Ml.	Mg.	Ml.	Mg.
Cl_2					1.12	3.545						
CO_2							1.12	2.20				
HCN							2.24	2.702	2.24	2.702		
HCl	2.24	3.646					2.24	3.646	2.24	3.646		
H_2S			1.12	1.704							1.12	1.704
NO			2.231	3.00								
NO_2			2.24	4.60			2.24	4.60				
NH_3	2.24	1.703										
SO_2			1.118	3.20			1.118	3.20			1.118	3.20
O_3						2.4						
$(CN)_2$							1.120	2.6008	1.120	2.6008		

Table 8

DATA ON CYLINDERS FOR COMPRESSED GASES

Style	AAA	B	C	D	E	F	G	H
Diameter inches	2	3¼	4½	4½	4½	5½	8½	9
Height inches	12	16	18	20	29	55	55	55
Capacity cu. in.	—	90	142	177	288	930	2380	2660
Capacity cu. ft.	—	.052	.082	.102	.166	0.537	1.375	1.54
Capacity cu. cm.	—	1474	2326	2900	4723	15252	39032	43624

The smaller cylinders from E to AAA have no threads on them to couple to fittings: they are connected to apparatus by a simple yoke with a hose connection.

Table 9

Correction Factors for Gas Volume

[Multiply observed volume of saturated gas by factor to correct to volume of saturated gas at 30 inches of mercury pressure (32° F.) and 60° F.[234]]

Temperature	Total Gas Pressure—Inches of Mercury												
	28.0	28.1	28.2	28.3	28.4	28.5	28.6	28.7	28.8	28.9	29.0	29.1	29.2
° F.													
99	0.825	0.828	0.831	0.834	0.837	0.840	0.844	0.847	0.850	0.853	0.856	0.859	0.863
98	.828	.831	.834	.838	.841	.844	.847	.850	.853	.856	.860	.863	.866
97	.831	.834	.838	.841	.844	.847	.850	.853	.856	.860	.863	.866	.869
96	.834	.838	.841	.844	.847	.850	.853	.856	.860	.863	.866	.869	.872
95	.837	.841	.844	.847	.850	.853	.856	.860	.863	.866	.869	.872	.876
94	.841	.844	.847	.850	.853	.856	.860	.863	.866	.869	.872	.876	.879
93	.844	.847	.850	.853	.856	.860	.863	.866	.869	.872	.876	.879	.882
92	.847	.850	.853	.856	.860	.863	.866	.869	.872	.875	.879	.882	.885
91	.850	.853	.856	.859	.862	.866	.869	.872	.875	.878	.882	.885	.888
90	.853	.856	.859	.862	.866	.869	.872	.875	.878	.882	.885	.888	.891
89	.856	.859	.862	.865	.868	.872	.875	.878	.881	.885	.888	.891	.894
88	.859	.862	.865	.868	.872	.875	.878	.881	.884	.888	.891	.894	.897
87	.861	.865	.868	.871	.874	.878	.881	.884	.887	.890	.894	.897	.900
86	.864	.868	.871	.874	.877	.880	.884	.887	.890	.893	.897	.900	.903
85	.867	.870	.874	.877	.880	.883	.887	.890	.893	.896	.900	.903	.906
84	.870	.873	.876	.880	.883	.886	.890	.893	.896	.899	.902	.906	.909
83	.873	.876	.879	.883	.886	.889	.892	.896	.899	.902	.905	.909	.912
82	.876	.879	.882	.885	.889	.892	.895	.898	.902	.905	.908	.911	.915
81	.878	.882	.885	.888	.891	.895	.898	.901	.904	.908	.911	.914	.918
80	.881	.884	.888	.891	.894	.897	.901	.904	.907	.910	.914	.917	.920
79	.884	.887	.890	.894	.897	.900	.904	.907	.910	.913	.916	.920	.923
78	.887	.890	.893	.896	.900	.903	.906	.910	.913	.916	.919	.923	.926
77	.889	.892	.896	.899	.902	.906	.909	.912	.916	.919	.922	.925	.929
76	.892	.895	.898	.902	.905	.908	.912	.915	.918	.921	.925	.928	.931
75	.894	.898	.901	.904	.908	.911	.914	.918	.921	.924	.928	.931	.934
74	.897	.900	.904	.907	.910	.914	.917	.920	.924	.927	.930	.933	.937
73	.900	.903	.906	.910	.913	.916	.920	.923	.926	.930	.934	9.36	.939
72	.902	.906	.909	.912	.916	.919	.922	.926	.929	.932	.936	.939	.942
71	.905	.908	.912	.915	.918	.922	.925	.928	.931	.935	.938	.941	.945
70	.907	.911	.914	.917	.921	.924	.927	.931	.934	.937	.941	.944	.947
69	.910	.913	.917	.920	.923	.927	.930	.933	.937	.940	.943	.947	.950
68	.912	.916	.919	.922	.926	.929	.932	.936	.939	.942	.946	.949	.952
67	.915	.918	.922	.925	.928	.932	.935	.938	.942	.945	.948	.952	.955
66	.917	.921	.924	.928	.931	.934	.938	.941	.944	.948	.951	.954	.958
65	.920	.923	.927	.930	.933	.937	.940	.944	.947	.950	.954	.957	.960
64	.922	.926	.929	.932	.936	.939	.943	.946	.949	.953	.956	.959	.963
63	.925	.928	.932	.935	.938	.942	.945	.948	.952	.955	.959	.962	.965
62	.927	.931	.934	.937	.941	.944	.948	.951	.954	.958	.961	.964	.968
61	.930	.933	.936	.940	.943	.947	.950	.953	.957	.960	.964	.967	.970
60	.932	.936	.939	.943	.946	.949	.953	.956	.959	.963	.966	.969	.973

[234] Formula used: Correction factor $= \frac{(P-E)(60+459.4)}{(t+459.4)(30-0.5170)}$

P = total gas pressure
E = vapor pressure of water at $t°$
t = temperature of gas (° F.).

Correction Factors for Gas Volume—*Continued*

[Multiply observed volume of saturated gas by factor to correct to volume of saturated gas at 30 inches of mercury pressure (32° F.) and 60° F.[235]]

Temperature	Total Gas Pressure—Inches of Mercury—Continued												
	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
°F.													
99	0.866	0.869	0.872	0.875	0.878	0.882	0.885	0.888	0.891	0.894	0.897	0.900	0.904
98	.869	.872	.875	.879	.882	.885	.888	.891	.894	.898	.901	.904	.907
97	.872	.876	.879	.882	.885	.888	.891	.894	.898	.901	.904	.907	.910
96	.876	.879	.882	.885	.888	.891	.895	.898	.901	.904	.907	.910	.914
95	.879	.882	.885	.888	.892	.895	.898	.901	.904	.907	.911	.914	.917
94	.882	.885	.888	.892	.895	.898	.901	.904	.907	.911	.914	.917	.920
93	.885	.888	.892	.895	.898	.901	.904	.908	.911	.914	.917	.920	.923
92	.888	.891	.895	.898	.901	.904	.907	.911	.914	.917	.920	.923	.927
91	.891	.894	.898	.901	.904	.907	.910	.914	.917	.920	.923	.926	.930
90	.894	.898	.901	.904	.907	.910	.914	.917	.920	.923	.926	.930	.933
89	.897	.901	.904	.907	.910	.914	.917	.920	.923	.926	.930	.933	.936
88	.900	.904	.907	.910	.913	.916	.920	.923	.926	.929	.933	.936	.939
87	.903	.907	.910	.913	.916	.920	.923	.926	.929	.932	.936	.939	.942
86	.906	.910	.913	.916	.919	.922	.926	.929	.932	.935	.939	.942	.945
85	.909	.912	.916	.919	.922	.925	.929	.932	.935	.938	.942	.945	.948
84	.912	.915	.919	.922	.925	.928	.932	.935	.938	.941	.945	.948	.951
83	.915	.918	.922	.925	.928	.931	.934	.938	.941	.944	.948	.951	.954
82	.918	.921	.924	.928	.931	.934	.937	.941	.944	.947	.950	.954	.957
81	.921	.924	.927	.930	.934	.937	.940	.944	.947	.950	.953	.957	.960
80	.924	.927	.930	.933	.937	.940	.943	.946	.950	.953	.956	.960	.963
79	.926	.930	.933	.936	.940	.943	.946	.949	.952	.956	.959	.962	.966
78	.929	.932	.936	.939	.942	.946	.949	.952	.955	.959	.962	.965	.968
77	.932	.935	.938	.942	.945	.948	.952	.955	.958	.961	.965	.968	.971
76	.935	.938	.941	.944	.948	.951	.954	.958	.961	.964	.968	.971	.974
75	.937	.941	.944	.947	.950	.954	.957	.960	.964	.967	.970	.974	.977
74	.940	.943	.947	.950	.953	.957	.960	.963	.966	.970	.973	.976	.980
73	.943	.946	.949	.953	.956	.959	.963	.966	.969	.972	.976	.979	.982
72	.945	.949	.952	.955	.959	.962	.965	.969	.972	.975	.978	.982	.985
71	.948	.951	.955	.958	.961	.965	.968	.971	.975	.978	.981	.985	.988
70	.951	.954	.957	.961	.964	.967	.971	.974	.977	.981	.984	.987	.991
69	.953	.957	.960	.963	.967	.970	.973	.977	.980	.983	.987	.990	.993
68	.956	.959	.962	.966	.969	.973	.976	.979	.983	.986	.989	.993	.996
67	.958	.962	.965	.968	.972	.975	.979	.982	.985	.989	.992	.995	.999
66	.961	.964	.968	.971	.974	.978	.981	.984	.988	.991	.995	.998	1.001
65	.964	.967	.970	.974	.977	.980	.984	.987	.990	.994	.997	1.001	1.004
64	.966	.970	.973	.976	.980	.983	.986	.990	.993	.996	1.000	1.003	1.007
63	.969	.972	.975	.979	.982	.986	.989	.992	.996	.999	1.002	1.006	1.009
62	.971	.975	.978	.981	.985	.988	.992	.995	.998	1.002	1.005	1.008	1.012
61	.974	.977	.980	.984	.987	.991	.994	.997	1.001	1.004	1.008	1.011	1.014
60	.976	.980	.983	.986	.990	.993	.997	1.000	1.003	1.007	1.010	1.014	1.017

[235] Formula used: Correction factor $= \frac{(P-E)(60+459.4)}{(t+459.4)(30-0.5170)}$

P = total gas pressure
E = vapor pressure of water at $t°$
t = temperature of gas (° F.).

Table 10

EMERGENT STEM CORRECTIONS TO READINGS OF OUTLET-WATER THERMOMETERS FOR DIFFERENT IMMERSIONS OF THERMOMETERS IN CALORIMETER

[Table applicable when temperature of inlet water is approximately equal to room temperature]

	Temperature Rise of Water	Temperature of Room					
		50°	60°	70°	80°	90°	100°
	° F.						
Thermometer immersed to 30° F.	10	+0.02	+0.03	+0.04	+0.05	+0.05	+0.06
	15	+.04	+.05	+.06	+.07	+.09	+.10
	20	+.06	+.07	+.09	+.11	+.13	+.15
Thermometer immersed to 40° F.	10	+.01	+.02	+.03	+.03	+.04	+.05
	15	+.03	+.04	+.05	+.06	+.08	+.09
	20	+.04	+.05	+.07	+.09	+.11	+.12
Thermometer immersed to 50° F.	10	+.01	+.01	+.02	+.03	+.04	+.05
	15	+.02	+.03	+.04	+.05	+.07	+.08
	20	+.02	+.04	+.06	+.07	+.09	+.11
Thermometer immersed to 60° F.	10	+.00	+.01	+.02	+.02	+.03	+.04
	15	+.00	+.01	+.03	+.04	+.05	+.06
	20	+.00	+.02	+.04	+.05	+.07	+.09

This table is not applicable if the emergent portion of the stem includes an enlargement in the capillary.

Instead of using the above table, it will probably be somewhat more convenient to make out a stem-correction table for the particular outlet-water thermometer that is to be used with the calorimeter, the data for this separate stem-correction table being interpolated from the above table.

Suppose, for example, the outlet-water thermometer to be used was one that was immersed to the 30° F. mark on the scale, and a stem-correction table were wanted for an 18° F. rise in temperature, then from the above table we obtain the following stem-correction table:

Stem Correction for Outlet-Water Thermometer No.—

[Table applicable when inlet water is approximately at room temperature, when thermometer is immersed to the 30° F. mark, and when the temperature rise is approximately 18° F.]

Inlet-water Temperature	Stem Correction	Inlet-water Temperature	Stem Correction
° F.	°	° F.	°
50	0.05	80	0.09
60	.06	90	.11
70	.08	100	.13

In the same way a table could be made out for any outlet-water thermometer by interpolation in the general table. The table so prepared would apply for the particular point to which the thermometer was immersed and for the particular rise in temperature with which the observer had chosen to work.

Table 11

Humidity Corrections in B.t.u.'s

Calculated on the Basis of 7 vols. Air, 1 vol. Gas and 6.6 vols. Products. Applicable when Air, Gas and Products are at the Same Temperature

Room temperature.	Depression of Wet Bulb Thermometer in Degrees Fahrenheit (Rapid Ventilation)														
	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
60	+0.1	+0.4	+0.7	+1.1	+1.4	+1.7	+1.9	+2.2	+2.5	+2.7	+3.0	+3.3	+3.6	+3.9	+4.1
65	0	+0.4	+0.7	+1.0	+1.4	+1.7	+2.0	+2.3	+2.7	+2.9	+3.2	+3.5	+3.8	+4.1	+4.4
70	−0.1	+0.3	+0.7	+1.0	+1.4	+1.7	+2.1	+2.4	+2.8	+3.1	+3.4	+3.7	+4.0	+4.3	+4.7
75	−0.2	+0.2	+0.6	+1.0	+1.4	+1.7	+2.1	+2.5	+3.0	+3.3	+3.7	+4.0	+4.3	+4.6	+5.0
80	−0.3	+0.1	+0.5	+0.9	+1.4	+1.8	+2.2	+2.7	+3.1	+3.5	+3.9	+4.3	+4.6	+5.0	+5.3
85	−0.6	0	+0.4	+0.8	+1.4	+1.9	+2.3	+2.8	+3.2	+3.6	+4.1	+4.6	+4.9	+5.4	+5.7
90	−0.8	−0.2	+0.3	+0.8	+1.4	+1.9	+2.4	+2.9	+3.3	+3.8	+4.3	+4.8	+5.2	+5.7	+6.1
95	−1.0	−0.4	+0.2	+0.7	+1.3	+1.9	+2.5	+2.9	+3.4	+4.0	+4.5	+5.1	+5.5	+6.0	+6.4
	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

L. R. M. '23.

HEATING VALUE TEST RECORD.

Place Bureau Stds. Date Oct 8 1913 Time 10 a.m. Gas Ptwn

Calorimeter No. J1209 Meter No. 6312 Thermometer No.: Inlet 57818 Outlet 57818

Gas line purged Yes/No Meter adjusted Yes/No Leak test Yes/No Water valve 65 Damper closed

Differential therm. corr'n. det'd Oct. 1 1913 (date). Last meter calibration Sept 4, 1913 (date).

	START.	END.
* Temp. of barometer	68°	68°
* Barometer reading	29.52	29.51
Certif. corr'n	−.01	
Temp. corr'n	−.10	
Corr'd barom. height	29.40	
* Pressure at meter (inches of water)	1.5	
Equiv. (inches of mercury)	.11	
Total gas pressure	29.51	
* Meter therm. reading	68.1	68.3
Certif. corr'n	−.3	
Meter temp.	67.9	
Reduction factor F	0.963	
* Psychrometer wet bulb	53.0	53.0
Psychrometer dry bulb	68.0	68.5
Humidity	35%	
* Temp. of products	69	
* Time of 1 meter rev.	52"	
Equiv. rate (cu.ft. per hr.)	6.9	

CONDENSED WATER COLLECTED.	TEST 1	TEST 2
Meter reading: start	18.1	19.4
" " end	19.1	20.4
Condensate (cc)	21.6	21.2
" per cu.ft. (60° 30 in.)	223	219
Average A	22.1	

NET HEATING VALUE	
Observed heating value average	644
Corr'n for heat loss	+ 1
Reduction to net (A × 2.3)	− 51
Net heating value	594

Certificate as correct.

E. F. M.

Observer

	SERIES No. 1.		SERIES No. 2.		SERIES No. 3.	
	INLET	OUTLET	INLET	OUTLET	INLET	OUTLET
Preliminary.	67.94	86.54	67.93	86.40	67.90	86.40
		50		45		45
Used in averaging.		50		49		48
		43		40		40
		36		43		39
		43		47		43
		54		50		49
	67.93	49	67.98	50	67.90	52
		50		41		50
		50		40		46
		47		48		42
		40		38		45
Supplementary.		49		41		46
	67.93	36	67.92	41	67.90	47
Average	67.93	86.46	67.93	86.45	67.90	86.45
Certificate corr'n	−18	−25				
Differential corr'n		−02	−18	−19	−18	−19
Emergent stem corr'n		+08				
Corrected temp.	67.75	86.27	67.75	86.26	67.72	86.26
Temp. rise T	18.52		18.51		18.54	
Water heated W	6.74		6.74		6.72	
No. of rev. of meter	2					
Meter calib. 1 rev. =	0.1006					
Gas volume V	0.2012					
Observed heating value $\frac{W \times T}{V \times F}$	644		644		643	
Corr'n for heat loss	+ 1					
Corr'n for atmos. humid	+ 4					
Total heating value	649		649		648	
Average	649 B.t.u. per cu.ft. (60° 30 in.).					

BUREAU OF STANDARDS
Form 268

CHEMICAL MICROSCOPY [1]

ADVANTAGES OF MICROSCOPICAL METHODS

If the term "chemical analysis" is construed in a broad sense, it covers determinations of properties and behavior as well as of composition. Most purely chemical data must ultimately be translated into comparisons of purity, costs, strength, or other aspects of the history or future performance of the material in question, but such interpretations are frequently indirect and inconclusive. The great advantage of microscopical methods in analytical chemistry lies in the directness of the information which they yield and the rapidity with which it is obtainable. The ability to deal with minute amounts of material is in most cases secondary to that of being able to observe the actual physical condition of the sample and the phenomena which it exhibits, in a vivid "close-up" rather than by inference.

A further advantage of the application of the microscope to analytical problems results from the fact that the sample itself is of necessity under direct examination, so that in most instances unsuspected and highly significant additional information, which might otherwise have been missed, is brought forth.

STUDIES OF SINGLE SUBSTANCES

As an aid to ordinary macroscopical analysis of single substances the microscope is employed in various ways. Single substances can be examined for purity and uniformity, and their physical state observed. Particle size and shape of powdered materials may be ascertained, as factors governing solubility, reactivity or suitability for pigments, fillers, abrasives, etc. Surface character of coatings, such as paints, glazes, platings, or enamels, may explain their failure better than data as to their constitution.

Identification of substances is rendered more positive by supplementing the analytical information by a determination of characteristic structural or optical properties, for which the microscope is the instrument *par excellence*. By utilizing published descriptions or by comparison with authentic "knowns" conclusive identification is frequently possible without the use of chemical reactions and without the need of separating the material from its surroundings or from a mixture.

[1] E. M. Chamot, Professor of Chemistry, Emeritus, Cornell University, and C. W. Mason, Professor, Chemical Microscopy, Cornell University.

Distinctive microscopical structure which serves as the basis for such identifications is particularly advantageous in the case of materials that are of highly complex chemical constitution, such as the plant and animal tissues of foodstuffs, textiles and paper fibers. In such examinations the recognition is based on characteristic morphological featurism supplemented in some cases by staining reactions. Familiarity with the appearances of the substances studied is essential; if in addition to identification the physical condition of the fibers or the process used in their preparation is indicated, further valuable information may be obtained.

Optical properties are a valuable means of identification, particularly in the case of crystalline substances. The latter are not usually distinguishable by form alone, but since some ten or twelve properties, about half of them numerical constants and the rest "positive" (+) or "negative" (−), are determinable, recognition is usually possible, provided the optical description of the substance appears in the published tables or has previously been determined by the analyst. These various optical tests serve for a classification which is analogous to the groupings, subgroupings, and successive reactions involved in qualitative analytical schemes, and the identification based on them is no less conclusive than that based on a series of chemical reactions.

Descriptions of all the common minerals are published in convenient tables [2] —an indispensable aid to the fullest analysis, for they permit the actual solid phase to be determined and not merely the ions which it yields after a rather violent "opening up" or solution process. In the case of inorganic salts the published data are less complete and only partially tabulated,[3] but the advantage of being able to ascertain the particular salt, hydrate, or allotropic form in hand, rather than the anions and cations only, makes optical analysis indispensable whenever this information is desired. Organic compounds are as yet largely undescribed optically, but any properties available [4] are doubly useful; in the absence of adequate data, checking the unknown against material of known purity may prove time and labor saving, especially if the chemical tests are inconclusive.

The actual examination of the optical properties of chemical substances is preferably carried out on material which has been powdered, or better, recrystallized on a microscope slide.

The following **properties of crystalline substances** are determined if observable:[5]

[2] Larsen and Berman, "Microscopical Determination of the Non-opaque Minerals," U. S. Geol. Survey Bull., 848 (1934); Winchell, "Elements of Optical Mineralogy," Part II (1927).

[3] Winchell, "The Optic and Microscopic Characters of Artificial Inorganic Substances." (John Wiley and Sons, New York, 1932); Fry, "Tables for the Microscopic Identification of Inorganic Salts," U. S. Dept. Agr. Bull., 1108 (1922); "International Critical Tables," Vol. I. (Refractive indices and crystal systems only.) Groth, "Chemische Krystallographie," 5 Vols. (Data not tabulated, but very extensive.)

[4] "International Critical Tables," Vol. I (1926), pp. 320–338. Mayrhofer, "Mikrochemie der Arzneimittel und Gifte," 2 Vols. (1928). Groth, "Chemische Krystallographie."

[5] For discussions of these properties and the methods of observing and describing them, see Chamot and Mason, "Handbook of Chemical Microscopy," Vol. I (1938), Chapter IX, especially pages 303 to 319. Winchell, "Elements of Optical Mineralogy," Part I (1928). Hartshorne and Stuart, "Crystals and the Polarising Microscope" (Arnold, London, 1934).

Phenomena of Crystallization.—Condition of crystals, as received. Action of solvents. Effect of heating. Growth of crystals from solution or from the melt. Evidence of allotropic transformations or double salt formation.

Geometrical Form and Characteristic Angles.—Study and correlation of different "views," of the simpler crystals, by means of drawings or models of cork or wax.

Doubly Refractive Character.—Isotropic substances (cubic system, or basal views of hexagonal and tetragonal systems) remain dark between crossed nicols, on rotating the stage.

Anisotropic or doubly refractive substances (all crystal systems except cubic) show "extinction" at 90° intervals, with intermediate positions of brightness. Pleochroism is shown by some colored anisotropic substances, as a change in color when the stage is rotated, only one nicol being used. Strongly doubly refractive substances show a change of shading, with one nicol.

Positions of Extinction.—Parallel or symmetrical, if a prominent crystal edge or diagonal is parallel to the cross hairs (which must represent the planes of vibration of the polarizer and analyzer) when extinction occurs. Oblique extinction (possible only in the monoclinic and triclinic systems) occurs if the position of extinction is oblique to the cross hairs. The angle between the crystallographic edge or direction used for reference and the nearest cross hair is called the "extinction angle."

Strength of Double Refraction.—The maximum difference of the values of refractive indices is a numerical measure of the strength of double refraction or "birefringence." The polarization colors, which follow the same series as those of thin films, give an approximate indication. For crystals of ordinary microscopic size and thickness, low order colors (grays and straw-yellow to orange) indicate weak double refraction; brighter colors, moderate to strong double refraction; and high order colors (pale pinks and greens, to grayish white) strong double refraction.

Refractive Indices.—Two values are obtainable for any anisotropic view of a crystal; different views may show different pairs of values. After turning to the position of extinction, the crystal is illuminated with polarized light (one nicol only) the plane of vibration of which is known, and the tests given below are applied. The value for the position of extinction 90° from the first is determined similarly. The highest and the lowest values, for all possible views, are of particular interest.

Interference figures serve to indicate whether the substance is uniaxial (hexagonal or tetragonal systems) or biaxial (orthorhombic, monoclinic, or triclinic systems), and whether its double refraction is positive (+) or negative (−). The plane of the optic axes, and the angle between them, are also indicated. A discussion of these phenomena and tests is beyond the scope of this chapter.

For the above determinations of properties a chemical or petrographic microscope is necessary; it should be provided with polarizer and analyzer nicol prisms, graduated centerable revolving stage, crosshaired eyepieces, and compensators such as a "1st order red" plate or a quartz wedge; a condenser for use in the examination of interference figures is also desirable.

Refractive index determinations [6] require a series of standard liquids of known indices. The sample is compared with these by immersing microscopic crystals in the various liquids and applying tests to ascertain whether its index of refraction is higher or lower, until one of the standards is found to match it. In determining the refractive indices of doubly refractive substances illumination with polarized light is essential, and the orientation of the crystal with respect to the direction of transmission and of vibration of the light must be specified, especially if the values are to be compared with those commonly designated as ϵ and ω for uniaxial, and α, β, and γ for biaxial substances.

The tests employed for comparing refractive indices are very simple and rapid: Particles of the unknown are immersed in a drop of one of the series of

[6] See "Handbook of Chemical Microscopy," Vol. I, Chapter XI, especially pp. 366–373.

standard liquids on an object slide, and covered with a cover glass. With the diaphragm of the substage condenser closed as far as possible, a narrow bright line ("Becke line") appears to bound the grains; this moves toward the sub-

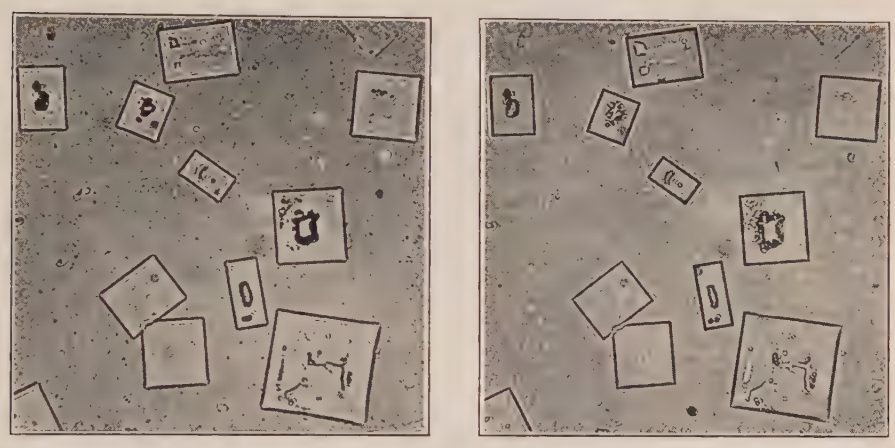


FIG. 389. The Becke Line. Sodium Chloride ($n=1.544$) in a Liquid of $n=1.540$. A—on focusing upward slightly; B—on focusing downward slightly.

stance of *higher* refractive index as the microscope is focussed *upward*, and toward the less refractive material as the focus is lower (see Fig. 389). If the condensor, with diaphragm fully opened, is focussed to give strongly convergent illumination and one edge of the diaphragm aperture is covered by the finger

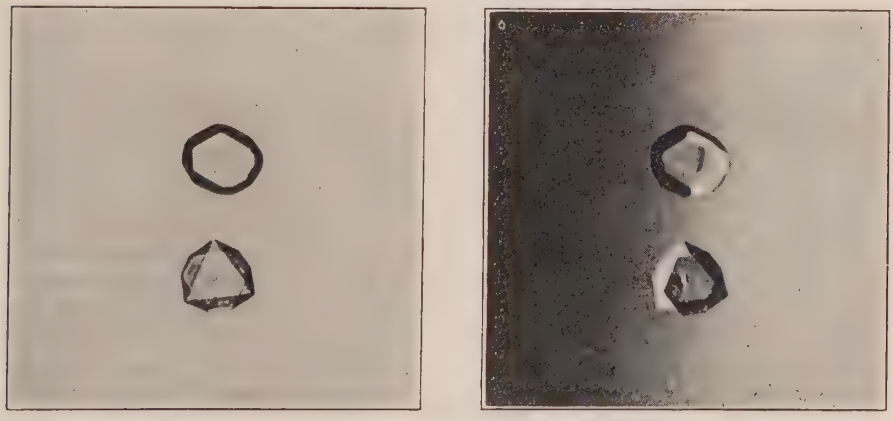


FIG. 390. Axial and Oblique Transmitted Illumination. The upper crystal has a higher refractive index than the mounting medium; the lower crystal, a less refractive index.

or a piece of paper, one side of the field will appear shaded. The boundary of the particles will also be darker on one side; if this shading is on the *same* side as the shadow in the field, the particle has a *higher* refractive index than the surrounding liquid, and *vice versa* (see Fig. 390).

STUDIES OF MIXTURES OF SUBSTANCES

As an aid in the examination of mixtures, the microscope is particularly useful; except in the case of gases and liquids or solid solutions, the constituents are seen, under sufficient magnification, to be merely "side by side," and their individual properties are available for purposes of identification, usually without the need for more than the "optical separation" which the microscope accomplishes.

Whatever information can be gathered from the microscopical examination of heterogeneous mixtures is clear gain, for it supplements the chemical findings and it helps to minimize the loss of evidence which is a consequence of the usual methods of preparation for analysis. In other words, the maximum amount of information should be obtained from the constituents while they are still discrete, and before they are merged together by the processes of solution, fusion, etc.

Furthermore, the mere recognition of the fact that a mixture is present is a guide to the interpretation of the analytical data, and the computation of the results in terms of the different substances actually present as separate phases is no longer a matter of conjecture or of arbitrary systems too often inconsistent with the facts. The conformity between calculated constituents and microscopically visible ones is an essential criterion in the analyses of rocks and ores consisting of mixtures of silicates, sulfides and other minerals.

Even though it may not be possible to separate and identify individually all the ingredients of a mixture, their nature may become apparent, in the light of further quantitative or qualitative analyses of the mixture as a whole.

In connection with sampling of mixtures for macroscopic analysis, either qualitative or quantitative, it is particularly important that any non-uniformity should be recognized, in order that proper precautions may be taken to insure a representative sample. A sample is not representative, however truly its composition may summarize that of the specimen as a whole, if in obtaining it the local variations of composition have been "averaged together" without knowledge or due appreciation of their existence or magnitude. Indeed, such segregations of ingredients may be of more significance than the general analysis, especially in the case of mixtures of powdered materials, or alloys, and they are likely to be missed unless the microscope is employed.

Separation of powdered mixtures [7] is often necessary and always advisable as a preliminary to qualitative or quantitative analysis. Hand sorting, under a low power magnifier or a Greenough binocular microscope, will be feasible for all but the finest powders. Glass rods drawn to hair-like fineness, a thin platinum wire, accurately pointed forceps, and capillary pipettes will be found useful for picking up small grains or shoving them into heaps. The rod or wire may be moistened or rendered slightly sticky by a trace of oil, balsam, vaseline or glycerine. Coherent aggregates such as rocks may need to be crushed fine enough to yield non-composite grains, but it is also possible, by means of a hard needle, a silicon carbide or diamond splint, or a fine dental chisel, to scrape off or dig out uncontaminated material sufficient for at least a microscopic or a spectroscopic qualitative analysis.

[7] See "Handbook of Chemical Microscopy," Vol. I, pp. 141–148.

For microanalysis, either non-microscopical or by means of qualitative tests carried out under the microscope, still smaller samples are feasible. Streaks of alloys or minerals, obtained by rubbing on a ground glass or silica plate, supply material in finely powdered form, with minimum injury to the specimen. "Chemical micrurgy" by means of the micromanipulator permits exceedingly minute particles to be dealt with, and is invaluable in the identification of "specks." [8]

Testing *in situ* is also a possibility, if separations are difficult; staining and etching reactions, such as are employed in the microscopical study of ores or alloys, enable the composition of the different grains of powdered or coherent specimens to be recognized, and further serve to reveal localized variation in the mixture.

HANDLING SMALL AMOUNTS OF MATERIAL [9]

Solid particles can best be handled by a glass rod or platinum wire, as mentioned above. If suspended in liquid, sedimentation or centrifugal separation will serve as a means of concentrating them. Fine capillary pipettes (Fig. 391)

FIG. 391.

made by drawing out glass tubing to about 1 mm. diameter, are useful for collecting sediments or transferring small quantities of liquid.

The **filtration** [10] of small drops may be readily accomplished by the Behrens-Hemmes method (Fig. 392). A small square of thick filter paper is placed close to the drop to be filtered, against the paper is gently pressed a capillary tube *F* whose lower end has been ground true and smooth. The paper with the tube in a vertical position is slowly pushed forward into the drop. The liquid rises into the tube by capillarity. In general it is best to first attach a rubber tube *R* to the tube *F* and draw up the liquid into the tube by gentle suction applied by the mouth to the mouth-piece *M*. The rubber tube is kept slightly bent as shown in the figure. At the moment of removal the tube is compressed be-

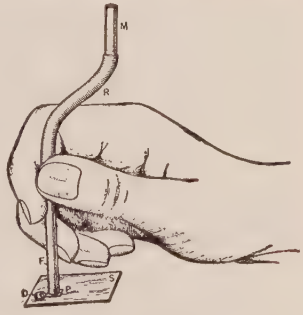


FIG. 392.

[8] Titus and Gray, Ind. Eng. Chem. (Anal. Ed.), 2, 368–71 (1930).
[9] "Handbook of Chemical Microscopy," Vol. I, pp. 141–5; Vol. II, p. 407.
[10] "Handbook of Chemical Microscopy," Vol. II, pp. 13–17.

tween the fingers and slightly stretched at the same time; this prevents the liquid from flowing out of the tube as it is lifted off the filter paper.

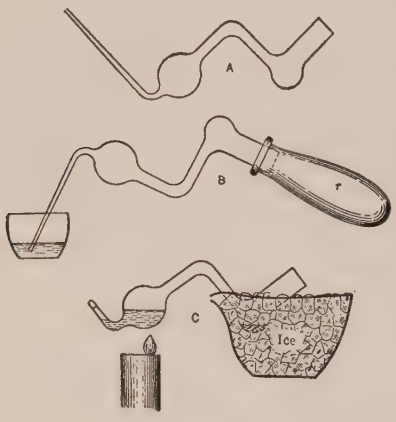


FIG. 393.

When merely the precipitate and not the liquid is required a narrow strip of filter paper may be introduced into the drop and the precipitate pushed into a little heap.

Decantation [11] will usually accomplish a perfectly satisfactory separation of liquid from a heavy precipitate. The object slide on which the drop rests must be scrupulously clean. If the end of a drawn-out glass rod or a platinum wire is introduced into the drop near its circumference and then moved outwards the liquid will follow the rod and if at the same time the slide is slightly tipped the liquid can be decanted from the precipitate.

Simple fractional **distillations** [12] can be successfully performed by means of the apparatus shown in Fig. 393, the successive fractions being removed from the receiver end of the distilling tube by means of a capillary pipette.

MICROSCOPICAL QUALITATIVE ANALYSIS [13]

Qualitative analyses are carried out under the microscope by means of crystallization and precipitation reactions, many of which are used in ordinary macroscopic analysis. Instead of basing the identification of a precipitate upon its color, upon the preceding steps in the analytical scheme, and upon its behavior toward the subsequent operations of the system, the microscopical form and optical properties of the precipitate are employed to characterize it. This necessitates the choice of reactions which shall yield practically specific appearances, and hence largely eliminates the need for following any systematic analytical scheme through a number of groups. Directness and rapidity are natural consequences of this procedure, for a precipitate when obtained is recognized as such, and is not dependent for its significance upon the efficacy of group separations.

[11] "Handbook of Chemical Microscopy," Vol. II, p. 10.

[12] "Handbook of Chemical Microscopy," Vol. II, pp. 18–20.

[13] For further discussion, see Chamot and Mason, "Handbook of Chemical Microscopy," Vol. II (1940), and the other books listed in the bibliography on page 2457.

Many of the reagents of microscopical qualitative analysis serve to show the presence of several different ions, and are commonly applied to small separate portions of the original solution. In special cases it may be desirable to separate or concentrate certain ingredients by means of some of the group reactions of ordinary qualitative analysis, and then to make use of the microscopical tests as a means of final identification of the constituents of the group precipitates.

The minute amounts of material involved in microscopical analysis also contribute to its rapidity; obviously, it is easier to dissolve a tiny fragment, or to filter or evaporate a drop or two of liquid than to deal with the usual quantities. In cases where the supply of sample is limited, microscopical methods of analysis are in order, and indeed may be indispensable. The sensitivity of the tests, although striking when expressed in absolute amounts, is no greater in terms of actual concentrations employed than that of the same reactions as used on a macroscopic scale. However, since it is possible to work with concentrates obtained from a small amount of a relatively dilute solution, the effective sensitivity may be very great.

Reagents are best kept as solids in small glass stoppered bottles, a drop of solution being made up when needed.

METHODS OF APPLYING REAGENTS

There is usually a specific method for applying the various reagents, depending upon the relative concentrations required and the nature of the reaction involved. In any case, however, actual precipitation is the criterion of a positive test; crystalline products appearing only after considerable evaporation has taken place are of little or no diagnostic value. Relatively dilute solutions are preferable, in order that separation of the reagent, the unknown, or various possible double salts may not mask the precipitate obtained, and in order that the latter may not be formed from such a highly supersaturated solution as to appear "amorphous" or unresolvable by the microscope.

The most important methods of applying reagents are as follows:

a. The drop of reagent is caused to flow into a drop of unknown solution on a microscope slide, by means of a small glass rod or platinum wire. The concentration gradient in the zone of mixing affords a considerable range of conditions, so that various regions of the preparation should be studied in order to observe a distinctive precipitate.

b. A solid fragment of the reagent is introduced into the test drop, either at the center, or sometimes at or near the circumference. When introduced at the center, solution is rapid, and if the reagent fragment is moderately large, excess of the reagent in high concentration is made effective. The reagent should be in small fragments—not finely powdered.

c. A solution of the reagent is drawn in a narrow channel across a dry film of the material to be tested. The unknown is dissolved in water or acid. A drop of the solution thus obtained is carefully evaporated to dryness upon a scrupulously clean object

slide, using great care to avoid heating the dry film too hot. A concentrated drop of the reagent is placed near the film and a narrow channel of the reagent is drawn across the dry film, the object slide being slightly tipped at the same time so as to feed reagent into the channel. Care must be taken that the reagent does not flood the entire drop. The reaction product is formed in the zone of contact between reagent and solid unknown. This method is used when the reaction product sought is relatively soluble, and when high effective concentrations of reagent and of unknown are necessary for its precipitation.

d. The addition of another ion giving a less soluble compound can be resorted to when an isomorphous series exists and the test as first performed has failed to yield a decisive test. One of the best illustrations is that of testing for lead and (or) copper with KNO_2. If no precipitate is obtained a Rb, Cs, or Tl salt can be added; the solubility of the compounds decreasing in the order named. The effect of such a procedure is to increase the sensitivity of the reaction.

e. The reagent is incorporated into a fiber (viscose, silk, wool, collodion, etc.) and the dry treated fiber is introduced into the test drop. This method is of great value in many cases. One of the best examples is testing for boron with a viscose rayon fiber impregnated with turmeric (curcumin).

f. When HF or fluorides are employed as precipitating reagents they are added to the test drop by either method *a* or method *b*, but special precautions are necessary. The object slide must be of non-siliceous material such as celluloid, cellophane etc., or an object slide may be protected by a coating of a hand impervious, transparent, colorless varnish. All objectives save the one to be used should be removed from the nose-pieces and this one protected by varnish, a protecting cell or drop of immersion oil and small cover-glass.

g. In certain specific cases, it is found to be advantageous to cause the reaction to take place in capillary tubes.

Reactions involving gas evolution (NH_3, or volatile acids) are most simply performed by placing the reacting substances in a tiny crucible (Fig. 394), over which is placed a glass slide bearing on its under surface a minute hanging drop of an appropriate acid or alkaline absorbent; the evolved gas is then tested for in this drop.

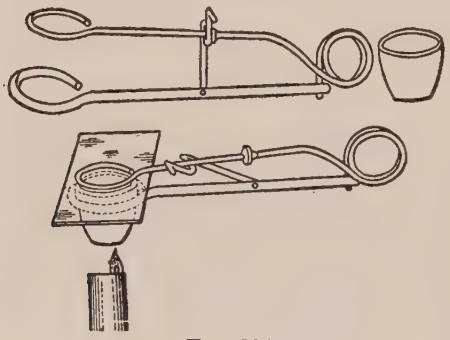


Fig. 394.

Fusions are carried out in a tiny platinum cup made from heavy foil; other high temperature reactions yielding sublimates are brought about in hard glass capillary tubes.

Reagents Used.—Some of the most useful group reagents of microscopical qualitative analysis are as follows:

Potassium Mercuric Thiocyanate, $K_2Hg(CNS)_4$.—Zn—feathery white crosses; Cd—colorless prisms with one end bluntly pointed; Co—blue prisms in radiating clusters; Cu—greenish yellow mossy dendrites or fusiform crystals; Zn+Cu—Zn crystals colored lavender, or brownish spherulites of radiating prisms; Zn+Cd, Ni, Mn—colorless arrowhead crystals; Au—golden yellow mossy dendrites; Fe—pink color or pink Zn or Cd crystals; Pb, Ag, Hg—very fine grained precipitate.

Cesium Chloride.—Sn—octahedra of Cs_2SnCl_6; Ag—fine octahedra of AgCl, recrystallizable from NH_4OH to give larger crystals; Pb—forked prisms of $PbCl_2$; Sb—hexagonal plates of $3CsCl \cdot 2SbCl_3$; Bi—hexagonal plates of $3CsCl \cdot 2BiCl_3$, or rhombic plates of $3CsCl \cdot BiCl_3$; Cd—hexagonal tablets or bipyramids of $CsCl \cdot CdCl_2$; Os, Ir, Pt, Pd—yellow to orange octahedra of Cs_2(Pt, etc.) Cl_6; Cu—yellow or orange prisms and plates.

Cesium Sulfate.—Al—colorless octahedra of cesium alum) Cr—purplish octahedra of cesium chrome alum; Ca—needles and oblique-ended prisms of $CaSO_4 \cdot 2H_2O$; Pb, Ba and Sr—fine granules of $BaSO_4$ or $SrSO_4$ (on recrystallization from conc. H_2SO_4, Ba gives feathery crosses and Sr dagger-shaped crystals).

Potassium Nitrite.—Co—fine yellow cubes of $3KNO_2.Co(NO_2)_3.1\frac{1}{2}\ H_2O$; Cu or Ni, +Pb—fine brown to black cubes of $2KNO_2 \cdot Cu(NO_2)_2 \cdot Pb(NO_2)_2$.

Silver Nitrate.—Colorless precipitates insoluble in HNO_3:

Cl^- or Br^-—granular, or very tiny octahedra; I^-—fine granular; BrO_3^-—tiny crosses and prisms; CN^-—granular or fine prisms.

Colorless precipitates soluble in HNO_3:

$C_2H_3O_2^-$—thin plates and prisms; NO_2^-—long slender needles, pale yellowish green; SO_4^{--}—rhombic tablets and prisms; CNO^-—fine needles and prisms on standing; IO_3^-—acicular and radiating crystals.

Colored precipitates:

AsO_4^{---}—red granular, small tablets; CrO_4^{--} or Cr_2O_7—red granules or pleochroic plates and acute rhombs; PO_4^{---}—yellow granular or tiny stars and crosses.

Barium Chloride.—Precipitates insoluble in HNO_3:

CrO_4^{--}, $Cr_2O_7^{--}$—yellow granules, tiny crosses; IO_3^-—granules, fine prisms and crosses; SO_4^{--}—granules, fine crosses and platelets.

Precipitates soluble in HNO_3:

BrO_3^-—prisms; CNO^-—spherulites and needles; CO_3^{--}—granules;

Ions yielding non-characteristic precipitates are not listed under the above reagents.

IDENTITY TESTS FOR ANIONS AND CATIONS

The most useful specific identity tests for the common anions and cations are as follows:

Cations

Na—pale yellow tetrahedra with uranyl acetate; many of the tetrahedra appear to be black because of total reflection. If the ratio Na : K is less than1 : 5, test usually fails. Na+zinc uranyl acetate yields pseudo-octahedra, very characteristic; presence of other alkalis or alkaline earths does not interfere with latter modification of test.

K—yellow or orange octahedra with H_2PtCl_6; colorless prisms with $HClO_4$. NH_3 must be absent, as it gives identical reactions.

NH_4—volatilization of NH_3. Treat with NaOH in crucible (Fig. 394) covered with an object slide carrying a hanging drop of very dilute HCl. Warm gently. Test hanging drop with H_2PtCl_6—yellow octahedra of $(NH_4)_2PtCl_6$.

Ca—fine needles, singly and in sheaves, oblique-ended prisms, and characteristic arrowhead twins, with dilute H_2SO_4. Prisms with tartaric acid. Very tiny octahedra with oxalic acid. Sr and Ba interfere if present.

Sr—fine granular precipitate with H_2SO_4, which when recrystallized from hot conc. H_2SO_4, yields dagger-shaped crystals. Ca and Ba must be absent. With oxalic acid, crystals similar to those of Ca.

Ba—feathery crosses on recrystallization from hot conc. H_2SO_4. Ca, Sr, Pb, Ag, must be absent. In concentrated acetic acid K_2CrO_4 yields a very fine granular or finely crystalline precipitate, Ca gives none, and Sr rarely unless the solution is made alkaline with NH_4OH. With oxalic acid, mossy aggregates.

Tests fail in mixtures of Ca, Sr and Ba. Separate Ca by extraction with boiling water, and Sr by dilute HNO_3. $BaSO_4$ remains insoluble; evaporation of aqueous extract gives crystals of $CaSO_4 \cdot 2H_2O$. Evaporation of HNO_3 gives residue of $SrSO_4$, which can be recrystallized from conc. H_2SO_4.

Mg—feathery stars developing into prisms, with PO_4^{---} and the test drop made alkaline with NH_4OH. Fe, CO, Ni, Mn must be absent.

Zn—feathery crosses with $K_2Hg(SCN)_4$. A very little Cd renders the crosses less feathery; more Cd leads to the formation of arrow heads. Ni modifies the crystals in a similar manner. Co colors the crystals blue, Cu lavender or brown, Fe pink or reddish brown. Oxalic acid forms short prisms and tablets.

Hg—globules of metallic Hg by heating in a closed tube with dry Na_2CO_3. Acidify a solution with HCl, boil with a fragment of Cu wire or Cu foil. Hg amalgamates with Cu. Heat coated Cu in closed tube—globules of Hg. Convert Hg into HgI_2 by iodine vapor—yellow and red crystals.

Hg(ous)—greenish "amorphous" ppt. with KI; white "amorphous" ppt. with HCl, turning black with NH_4OH; dark red granules or stars with $K_2Cr_2O_7$ in drops strongly acidified with HNO_3.

Hg(ic)—red HgI_2 with KI, soluble in excess; colorless feathery crosses with $Zn(C_2H_3O_2)_2$ and KSCN.

Al—octahedra with Cs_2SO_4. Excess of H_2SO_4 must be avoided.

Sn—convert to $SnCl_4$; add CsCl—tiny colorless octahedra. With oxalic acid, stannous salts give oblique ended prisms and skeletal forms; stannic salts give no precipitate.

Pb—yellow hexagonal plates with KI. Forked prisms with HCl. Brown or black cubes or tablets with KNO_2 and $Cu(C_2H_3O_2)_2$ in acetic acid solution.

Sb—hexagonal plates with CsCl; Bi gives hexagons unless the CsCl is in excess. Evolution as SbH_3 and blackening of $AgNO_3$ crystal; As must be proved absent by evolution of AsH_3 with Al and KOH; H_2S, H_3P interfere.

Bi—hexagonal plates with CsCl; rhombic plates with excess. Small prisms with Na_2SO_4 and H_2SO_4.

Cr—faintly purplish octahedra with Cs_2SO_4, when Cr is present as $Cr_2(SO_4)_3$. Conversion to CrO_4^{--} by evap. with HNO_3 and $KClO_3$ and subsequent testing with $AgNO_3$ gives pleochroic Ag_2CrO_4. When Cr is present as a compound of CrO_3, treat with NaCl and conc. H_2SO_4 in crucible with cover slide carrying a hanging drop of NH_4OH. Heat carefully; CrO_2Cl_2 is evolved. Evaporate hanging drop; test with $AgNO_3$ for CrO_4^{--}.

Mn—as MnO_4^- by oxidation with $(NH_4)_2S_2O_8$(+$AgNO_3$ as catalyst). Or fuse with Na_2CO_3 and KNO_3 to give green Na_2MnO_4, purple on acidification.

Mn^{++}—long twinned prisms and six-armed radiates with $H_2C_2O_4$. Excess of NH_4 salts and mineral acids must be absent. Masked by many other cations.

Fe—blue color and precipitate with $K_4Fe(CN)_6$. Red color with KSCN if Fe^{+++}.

Co—blue prisms with $K_2Hg(SCN)_4$. Excess of Fe or Ni interferes. When Zn is present, blue feathery crosses or arrow-heads; organic acids interfere. KNO_2 and $HC_2H_3O_2$—yellow cubes; Cu, Pb, Ni, Fe interfere.

Ni—fine pink needles with dimethylglyoxime. Tiny brown cubes with KNO_2, $Pb(C_2H_3O_2)_2$ and $HC_2H_3O_2$; Cu, Co must be absent; excess of Fe interferes.

Cu—greenish yellow mossy dendrites with $K_2Hg(SCN)_4$ (lavender or black spherulites if Zn is present). Tiny black cubes with KNO_2, $Pb(C_2H_3O_2)_2$ and $HC_2H_3O_2$ (Ni, Co must be absent). Yellow prisms or orange plates with CsCl.

Ag—"amorphous" precipitate or tiny octahedra with HCl, larger on recrystallization from NH_4OH. Red pleochroic acute rhombic plates with $K_2Cr_2O_7$. Red granules and hexagonal tablets with AsO_4^{---}.

SCHEME FOR THE QUALITATIVE ANALYSIS OF COMMON NON-FERROUS ALLOYS

The following tabulation [14] may prove useful for the systematic qualitative analysis of alloys or mixtures containing salts of the metals indicated.

Dissolve in concentrated HNO_3. Evaporate to a syrupy consistency or to a moist mass on water bath. Do not carry to complete dryness. Add water and again evaporate. Extract with *warm* water. Filter.

Residue A As; Sb; Bi; Sn—(Traces of Pb; Cu etc.) Remove a little of the residue and test it for As by conversion in H_3As.

Dissolve the remainder of Residue *A* in aqua regia. Divide into three parts.

1. Test with CsCl. Or reduce with metallic Fe to $SnCl_2$ and test for Sn.
2. If Sn is absent test for Sb with CsCl; if Sn is present convert into potassium antimonate and test with Na = Sodium antimonate.
3. Test with CsCl and confirm by conversion into sodium or potassium bismuth sulfate.

Filtrate I Add NH_4Cl and NH_4OH Filter = Filtrate III.

Precipitate *B*.

Precipitate B Fe; Cr; Al; Pb; Hg—Dissolve in the least possible volume of dilute HCl. Add NaOH in excess. Add Na_2O_2, boil, filter = Filtrate II.

Precipitate *C*.

Precipitate C Hg, Fe—Dissolve in dilute HCl. Divide into two parts.

1. Test for Hg with KI. Or treat with metallic copper, sublime the Hg and convert the globules into HgI_2 with iodine.
2. Test for Fe with KSCN or $K_4Fe(CN)_6$.

Filtrate II Al; Pb; Cr—Acidify with acetic acid. Divide into three parts.

1. Test for Pb with KI after adding HNO_3.
2. Test for CrO_4^{--} with $AgNO_3$. (Silver acetate may be precipitated.)
3. Precipitate all the lead as $PbSO_4$. Centrifuge. Concentrate. Test for Al with Cs_2SO_4.

Filtrate III Mn; Ni; Co; Zn—Add H_2O_2, boil and filter = Filtrate IV. Precipitate *D*.

Precipitate D Mn; Co; Ni—Divide into three parts.

1. Fuse with Na_2CO_3; green color = Mn. Or test for Mn with sodium bismuthate.
2. Dissolve in HCl and test for Ni with dimethylglyoxime.
3. Dissolve in HCl and test for Co with $K_2Hg(SCN)_4$. Or test with sodium nitrite.

Filtrate IV Cu; Zn; Cd; Ni; Mg—Acidify with HCl. Add Na_2SO_3 and NH_4SCN, boil and filter = Filtrate V. Precipitate *E*.

Precipitate E Cu—Dissolve in HCl. Test for Cu with $K_2Hg(SCN)_4$.

Filtrate V Zn; Cd; Ni; Mg—Add NH_4OH in slight excess. Divide into three parts.

1. Acidify with HCl. Test for Zn, Cd, with $K_2Hg(SCN)_4$.
2. Test for Ni with dimethylglyoxime.
3. Add HNa_2PO_4. Decant, filter or centrifuge. Dissolve the precipitate in the least amount of HCl. Reprecipitate the Mg as $NH_4MgPO_4 \cdot 6H_2O$ with NH_4OH. Or add $NaC_2H_3O_2$ and $HC_2H_3O_2$ and test with $UO_2(C_2H_3O_2)_2$.

Anions

$B_4O_7^{--}$—rose color on turmeric-viscose fiber, changing to blue with alkali.

CO_3^{--}—CO_2 evolved on acidification. Fine granular ppt. becoming rhombohedral, with $Ca(C_2H_3O_2)_2$.

[14] Slightly modified from method of Whitmore and Schneider, Ind. Eng. Chem. (Anal. Ed.), **2**, 173 (1930).

NO_3^-—radiating needles with nitron sulfate.
NO_2^-—yellow cubes with K^+ and Co^{++}, and $HC_2H_3O_2$.
CN^-—HCN evolved on acidification. Tiny prisms with $AgNO_3$.
SCN^-—red color with Fe^{+++}. Feathery crosses with Zn^{++} and Hg^{++}.
$Fe(CN)_6^{----}$—blue ppt. with Fe (-ous or -ic), brown with Cu.
$Fe(CN_6)^{---}$—blue ppt. with Fe^{++}.
PO_4^{---}—tiny yellow 3-armed stars with $AgNO_3$. Feathery rosettes and prisms with Mg^{++}, NH_4OH and NH_4Cl. Tiny rounded octahedra with ammonium molybdate.
AsO_4^{---}—tiny red granules and hexagonal tablets with $AgNO_3$. Reactions as for PO_4^{---}, above.
AsO_2^-—small yellow granular disks with $AgNO_3$.
SO_4^{--}—needles and oblique-ended prisms with Ca^{++}. Rhombs with Ag^+. Fine granules and stars with Ba^{++}.
SO_3^{--}—evolution of SO_2. Reducing action, with consequent oxidation to SO_4^{--}.
$S_2O_3^{--}$—rhombic plates and sheaves of fine needles, with $Pb(C_2H_3O_2)_2$.
S^{--}—evolution of H_2S. Oxidation to SO_4^{--} with Br_2.
CrO_4^{--}, $Cr_2O_7^{--}$—red pleochroic acute rhombic plates; imparts red or orange color and pleochroism to co-precipitated Ag_2SO_4.
Cl^-—tiny octahedra with $AgNO_3$. Crosses with $TlNO_3$. Prisms with $Pb(NO_3)_2$. CrO_2Cl_2 evolved on warming dry material with H_2SO_4 and $K_2Cr_2O_7$, identified as CrO_4^{--} in hanging drop by $AgNO_3$.
Br^-—reactions similar to Cl^-. Br_2, evolved with $(NH_4)_2S_2O_8$ or $KMnO_4$, gives fine needles in hanging drop of *m*-phenylenediamine HCl solution.
I^-—yellow hexagonal plates with $Pb(NO_3)_2$. Red granules with $Hg(NO_3)_2$. I_2, evolved with $(NH_4)_2S_2O_8$, gives blue color with starch in same or in hanging drop.
ClO_3^-—reduction to Cl^- by SO_3^{--}. Yellow ClO_2 evolved on moistening dry material with conc. H_2SO_4.
BrO_3^-—crosses and prisms with $AgNO_3$. Br_2 on reduction with hydrazine or hydroxylamine sulfate.
IO_3^-—fine acicular crystals with $AgNO_3$. I_2 on reduction.
ClO_4^-—orthorhombic prisms with K^+, colored purple if trace of MnO_4^- is present.
MnO_4^-—purple color in solution, and in crystals of $KClO_4$.

The reactions listed above, while reliable in simple mixtures, may be interfered with by the presence of certain other substances. In such an event alternative tests or preliminary separations may be necessary.

ANALYSIS OF MATERIALS OF UNKNOWN COMPOSITION

A crystallographic examination should always be carried out. It is particularly important that the optical properties be determined even if the examination be directed merely to ascertaining whether the refractive indices are high or low and whether the material is isotropic or anisotropic.

When the material is isotropic its identification will, as a rule, be more readily accomplished by first testing for anions. When the material is anisotropic no general rule can be formulated. Reactions which seem most likely to yield conclusive information should be tried first. Each test should be so chosen and performed as to serve as a guide for the next step to be taken.

Formal schemes of analysis are not particularly advantageous, especially if the presence or absence of certain elements only is to be ascertained. Systematic procedures are largely based on those of macroscopic qualitative analysis.

Failure to obtain a positive test or one recognizable as due to any one of the ions sought may be due to a number of causes.

I. The reagent may be yielding a precipitate with the ion of opposite sign.

II. The test drop or the reagent drop may be too concentrated.

III. The test drop may not have the correct pH.

IV. Ions other than that being sought may interfere with the reaction. A change in crystal habit may result.

V. The precipitate formed may be masked by the precipitation of other compounds.

VI. The substance sought may be present in an amount below the sensitivity of the test.

VII. The substance sought may be present in a complex ion, in which its presence cannot be revealed by the reagent used. In order that the test may succeed the complex must be destroyed.

MICROSCOPICAL QUANTITATIVE ANALYSES [15]

In the analysis of heterogeneous mixtures the microscope is particularly valuable when the ingredients are of a complex chemical character, and when the ordinary methods of analysis yield data which do not directly indicate the composition in terms of the constituents of which the mixture is made up. Determinations of elements or ions by purely chemical means, although carried to several decimal places, may not yield as many *significant* figures as the less precisely quantitative microscopical methods, because of the hair-splitting assumptions often necessary before the results can be computed to give the information which is ultimately sought. This is particularly true in the case of starches, meals, flours; adulterated spices, cocoa, drugs and other food products; mixtures in which an undue proportion of naturally associated impurities is present; paper pulps, fabrics, felts; ore concentrates, refractories, rocks, alloys, explosives, etc.

In order that microscopic quantitative analyses may be applicable to the material, the following criteria should be satisfied:

1. The components must be easily distinguishable in the mixture, or they must be rendered so by special preparation or illumination technique.

2. The observed components must bear a reasonably constant relationship to the chemical or physical properties sought by the analysis.

[15] "Handbook of Chemical Microscopy," Vol. I, Chap. XIV.

3. If weight percentage composition is sought, the specific gravities of the components must be practically identical, or they must be known, or standard mixtures of known weight percentage composition must be available for comparison.

4. The sample must be representative, and satisfactory checks must be obtainable from duplicate determinations and from samples with known composition.

Preparation methods must be appropriate to the character of the sample. Powdered materials should be uniformly mixed and evenly distributed, without segregation of the different ingredients. This is usually best accomplished by suspending the material in a viscous liquid, such as glycerine or a heavy oil, spreading a drop on the slide, and covering with a cover-glass. By choosing a mounting medium with a refractive index nearer to one of the components than to another, their outlines may be made to appear distinctly different and thus aid rapid recognition. Examination between crossed nicols may accentuate differences between the ingredients. In food work ingredients, such as starch, which are not essential to the analysis and which obscure the significant tissue particles may be eliminated by chemical treatment. Paper fibers in mixtures are commonly stained by Herzberg's reagent, which selectively colors pure cellulose (rag) purplish red; purified cellulose (chemical wood, esparto) blue; and lignified cellulose (ground wood) yellow. Alloys are polished and etched to bring out the different solid phases; mineral mixtures may be examined in powdered form, but are frequently surfaced or sectioned.

In any microscopical analysis a number of fields, usually taken from different preparations, should be studied. Few materials are microscopically uniform, either in structure or composition, and this is particularly true the higher the magnification, the smaller the field, or the coarser the grain of the sample. Any data, such as counts or measurements, should be based on a considerable number (usually hundreds) of particles; the average values will then be consistent even when wide local variations occur. Individual counting tallies for each constituent are invaluable for such work, as labor savers.

It should be borne in mind that the ingredients sought in the analysis need not be those visible in the specimen, provided the relation between structure and composition is known. For example, carbon in steel may be estimated microscopically to about 0.1% (although no free carbon is present) by taking advantage of the fact that pearlite, visible as a distinct constituent, has a known carbon content of 0.8%, so that a steel containing 50% pearlite would have 0.4% C.

ANALYSIS BY ESTIMATION

If a specimen is prepared so as to render its components indubitably recognizable, it is frequently possible to estimate its composition with reasonable accuracy. Ideally, the constituents of the mixture should be of approximately equal fineness and specific gravity, lest coarse or bulky material be overestimated. An accuracy of $\pm 10\%$ of the proportion of each component is usually possible with simple binary or ternary mixtures; practise on series of similar constitution enables the observer to obtain results comparable with those based on systematic counting or measurements.

Comparisons with mixtures of known percentage composition lend further accuracy to estimation analysis; if a series of standards is available it is usually fairly easy for even the inexperienced observer to decide the value for the unknown. Permanent preparations or photomicrographs are useful as reference standards, but a comparison microscope or comparison eyepiece, which permits the unknown and the standard to be viewed simultaneously in the same field, is a great aid.

ANALYSIS BY COUNTING PARTICLES

The great majority of microscopical quantitative analysis of powdered mixtures are based on some form of counting procedure. Such numerical methods are preferable to estimations (even though slower), if several components are present, if there is an unavoidable tendency to over-estimate certain ingredients, if the particles are not uniform in size, or if such high magnification is necessary that the resulting small fields are not individually representative.

Ordinarily several hundred particles are counted, in fields systematically taken from more than one slide. If the particles vary in size, they are "weighted" in terms of their apparent volume.

Counting one constituent only is a feasible means of microscopical analysis, provided similar counts are carried out on the same quantity of material of known composition, as a basis for numerical comparison. The number of particles of a certain component in a definite amount of a mixture is frequently used as a measure of its quality. In the food industries especially, such determinations serve for control and inspection, furnishing information unobtainable by other means.

Seed hairs or bran particles in flour,[16] hulls in rice bran,[17] organisms in water,[18] molds in tomato products,[19] are thus determined.

[16] Keenan and Lyons, U. S. Dept. Agr. Bull., 938 (1922). Keenan, U. S. Dept. Agr. Bull., 1130 (1923).

[17] A. O. A. C., "Methods of Analysis" (1925), p. 122.

[18] Whipple, "Microscopy of Drinking Water" (1927), pp. 95, 123.

[19] Howard, U. S. Dept. Agr. Bull., 581 (1917); A. O. A. C., "Methods of Analysis" (1925), pp. 222–3; Jour. A. O. A. C., **6**, 146 (1922).

The determination of cocoa shells in cocoa is a typical example.[20] A 2 mg. sample is mounted in a clearing solution on a slide, and after it becomes sufficiently transparent the total number of shell fragments is counted. By comparing with similar counts on mixtures having known shell content, adulteration up to 10% may be determined with an agreement of one or two %.

Various means are employed for insuring that the same quantity of material shall be taken for each count: weighing a few milligrams directly on the slide; measuring the dry powdered material by volume; pipetting a definite volume of a suspension carrying a known concentration of the sample; or using hollow slides or cells of definite volume (see Fig. 395). The particles in the entire preparation must be counted, unless the distribution is practically uniform and the area over which the material is spread is kept the same for all preparations by using cells of definite area or definite thickness. Under these latter circumstances counts or small fractions of the entire area of the preparation, as defined by diaphragms or co-ordinate rulings in the eyepiece, or markings on the slide, are representative of the composition as a whole.

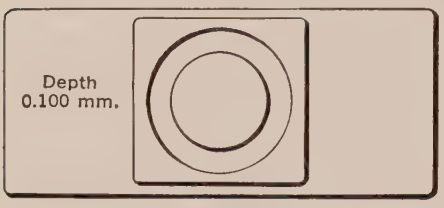


Fig. 395. Howard Counting Cell.

Whether the entire area or several fields distributed over it are counted, a mechanical stage for systematic movement of the preparation is almost indispensable.

The average number of particles per field or the total for a number of fields, preferably based on several different known mixtures, is plotted against the percentage composition or incorporated into a formula which serves to give the composition of any unknown mixture.

The ratio existing between the different constituents of natural mixtures is often characteristic, especially in food and drugs, any abnormal deficiency or excess of a typical tissue element being suspect. An analytical method involving ratios [21] makes use of a reference substance (usually lycopodium powder) which is added in definite amount to the unknown and in equal amount to a sample having known percentage composition. Without any precautions as regards the measurement of the preparation, counts of the particles in question and of the reference substance are made, the ratio between them being dependent upon the composition of the sample being analyzed.

Counting all constituents is preferable in most analyses of powdered materials, since known standards, measurements of the sample, and uniform size of preparation or of field are thus rendered unnecessary. Such methods are especially applicable to mixtures of several different components, such as papers, or powdered minerals. The counts should take into consideration the size as well as the number of the particles; the results will be in terms of percentage composition by volume unless the specific gravities of the ingredients are substantially equal, or are used to compute weight per cent.

[20] Silberberg, Jour. A. O. A. C., **6**, 98 (1922); Pease, idem, **7**, 141 (1923), **8**, 176 (1924); A. O. A. C., "Methods of Analysis" (1925), pp. 347–8.

[21] Wallis, Analyst, **41**, 357 (1916); "Analytical Microscopy" (1923), Chap. XI. Mason, Analyst, **58**, 440 (1933); Griffiths, *ibid.*, **62**, 510 (1937).

The analysis of a powdered mixture of quartz and feldspars, as used in ceramics, is an example of this type of method. Various schemes have been devised to aid in differentiating the particles of quartz, orthoclase, and plagioclase.

a. Vitrification of the feldspars by rapid fusion, without affecting the quartz, followed by mounting in a liquid of the same refractive index as that of the fused material, and comparison with a series of standard samples.[22]

b. Mounting of the untreated mixture in a liquid of refractive index 1.540 which is above feldspar and below quartz.[23]

c. Chemical differentiation, by exposure to HF vapor, which roughens the feldspars and leaves quartz clear, then treatment with $Na_3Co(NO_2)_6$ solution, which colors the orthoclase yellow.[24] About 200 grains, on each of three slides prepared by one of the above methods, are counted for the analysis.

Mixtures of gypsum and anhydrite are analyzed similarly, by mounting in a medium of refractive index 1.550, which is near that of gypsum; this serves to render the gypsum particles faint and transparent, while those of anhydrite are boldly outlined [25] (see Fig. 396).

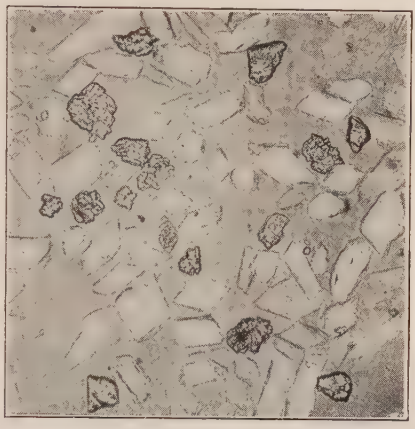


Fig. 396. Mixture of Ground Gypsum and Anhydrite, mounted in a liquid of refractive index near that of Gypsum.

Ore concentrates, if of complex mineral composition, are advantageously analyzed by the microscope, particularly since the actual amounts of the different minerals, rather than of elements that may occur in several, are sought. Composite grains, and the effectiveness of grinding and separation, are also recognized. The material is spread over a surface that is marked off in squares, and counted systematically, the size of the grains being taken into account.[26] A moderate magnification, such as is obtainable with a Greenough binocular microscope, is sufficient.

Paper fiber analysis is carried out by an analogous method, after pulping and staining with Herzberg's reagent. The fibers are tallied in terms of their length, measured with reference to the diameter of the field. An alternative method ("dot-count") is based on counts taken as the preparation is moved beneath the microscope. Every fiber any portion of which passes beneath a given point (dot or cross hairs) in the field is tallied, the longer ones thus being given proper emphasis. Counts in different places and directions on the preparation, dealing with at least 200 fibers on each of three slides, are customary.

[22] Booze and Klein, Jour. Amer. Ceram. Soc., **6**, 698 (1923).
[23] Insley, ibid., **10**, 651 (1927).
[24] Gabriel and Cox, Amer. Mineral, **14**, 290 (1929).
[25] Larsen, Proc. A. S. T. M., **23** I, 236 (1923); Gardner, idem, **26** I, 296 (1926).
[26] Coghill and Bonardi, Bur. Mines. Tech. Paper 211 (1919).

ANALYSES BASED ON MEASUREMENTS OF AREA

Areal and linear analysis depends on the fact that if a section is taken through an aggregate of heterogeneous material, the intercepts of the various ingredients in the plane of the section, or in a line across it, correspond to their respective percentages by volume. The specimen should be in compact form, so as to be surfaced or sectioned easily by cutting or grinding; alloys, rocks, refractories, etc. are suitable for such preparation. If powdered mixtures, such as ore concentrates, are to be dealt with they should be embedded in sealing wax or other cementing material, and the aggregate surfaced for measurement.

The areas of the constituents intersected by the plane of the specimen are conveniently measured on a drawing traced on co-ordinate paper by means of a drawing camera ("camera lucida"). A number of fields must be drawn, especially if the material is coarse grained or not mixed uniformly. Photographs (provided they represent enough area) may be cut out along the boundaries of the various ingredients, and the respective areas totalled by weighing the pieces of paper. Estimation or comparison with a series of known samples is often feasible as a time-saver.

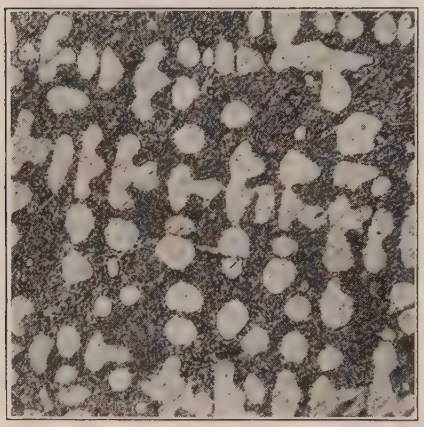


FIG. 397. Cast Copper, Containing about 0.25% Oxygen as $Cu-Cu_2O$ Eutectic (dark). Vertical illumination.

Linear analysis may be carried out on drawings or photographs; the intercepts are easily determined by marking off those of each ingredient on a separate strip of paper, the total lengths finally being measured by a ruler. Special mechanical stages are available, for moving the specimen across the field of the microscope. An individual screw is used for the movement of each ingredient, the corresponding total movements being shown on separate graduated scales. The total distance measured should be 100–200 times the diameter of the average sized grains.

The volume percentage composition furnished by areal or linear analyses will represent the percentage composition by weight only in case the specific gravities of the ingredients are practically identical. Otherwise, the volume per cent of each component must be multiplied by its specific gravity, and the resulting ratios converted to weight per cent. Such a calculation gives the relative amounts of the different solid ingredients, but not necessarily the chemical analysis of the sample. If these ingredients are of known chemical composition, the analysis of the mixture may be computed in terms of elements or radicals if desired, but this is not ordinarily of direct importance in work where areal analysis is used.

In the analysis of alloys it is sometimes desirable to ascertain the per cent of a given element, such as oxygen or carbon, which is present in combination

as an oxide, carbide, or eutectic of definite composition. In such a case, the volume per cent of the compound is multiplied by the per cent of the required element contained in it.

Examples of applications of areal methods of analysis are: oxygen in copper [27] (see Fig. 397), composition of alloys,[28] ores,[29] and rocks.[30]

DETERMINATION OF PHYSICAL PROPERTIES

In addition to the optical constants mentioned above, various other properties may be studied microscopically on minute amounts of sample. Melting and transition points are determined by means of a hot or cold stage,[31] which permits the temperature of the specimen to be controlled and measured while it is being observed under the microscope.

If the substance studied is doubly refractive (as most solids are) its melting may be observed with great sharpness by means of crossed nicol prisms, for the solid will appear bright against the dark field, and will disappear on fusion; a range of melting is also easily observed. For these reasons the melting points obtained by a hot stage are likely to be slightly lower than those by the capillary tube method.

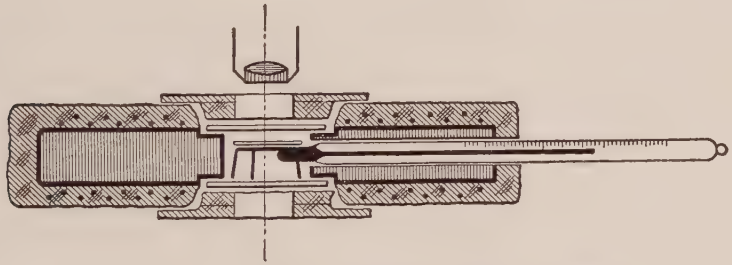


FIG. 398. Section of Electrically Heated Stage.

Electrically heated stages are preferable; temperatures may be regulated by a rheostat, over a range up to 400° or more. A thermometer (preferably a small Anschütz) or a thermocouple is used to measure the temperature; it is essential that it be placed as near as possible to the object under observation, and that the temperature within the stage show a minimum of local variations.

[27] Bardwell, Bull. Amer. Inst. Min. Eng., **79**, 1429; Tr. A. I. M. M. E., **46**, 742 (1913).
[28] Mathewson, Chem. Met. Eng., **11**, 619 (1913); Logan, idem, **11**, 668 (1913); Polushkin, Tr. A. I. M. M. E., **71**, 669 (1925).
[29] Thompson, Jour. Geol., **38**, 193 (1930).
[30] Alling and Valentine, Amer. Jour. Sci., **14**, 50–65 (1927).
[31] "Handbook of Chemical Microscopy," Vol. I, pp. 198–209.

It may be necessary to calibrate the stage or thermocouple by the use of substances having known melting points. A simple type of hot stage (see Fig. 398), that may be constructed by any competent mechanic, consists of a block of aluminum about 70×100×12 mm., perforated by an opening 20 mm. in diameter. The top and bottom surfaces are recessed to receive thin glass windows, and a hole is drilled in one edge for the insertion of the thermometer. About 2 meters of No. 20 (B. & S.) nichrome wire serves as the heating element; it is wrapped on in several layers, each insulated by asbestos paper. In applying the insulation, space is left for the insertion of the glass windows, which can be covered with a perforated sheet of asbestos board. The sample to be studied is mounted between two 18 mm. cover glasses, and supported on a tiny wire tripod in the center of the heating chamber, practically in contact with the thermometer.

Measurements with the microscope [32] are frequently employed in chemical work, and are practically indispensable in dealing with fine or irregular structures, fibers, coatings, or particles below the range of testing sieves.

The most widely used procedure employs a scale mounted within the eyepiece so as to appear superposed on the microscopic image. Since the value of the divisions of such a scale will vary with the magnification employed, it must be determined by comparison with a stage micrometer. The objective, eyepiece, and tube length used must be recorded, and maintained in any subsequent measurements, if the calibration is to be applicable.

Measurements of drawings, photomicrographs, or images projected on a screen may be made by establishing the scale of the enlarged image; this is done by replacing the specimen by a stage micrometer scale, and tracing its divisions enlarged to the same extent.

Particle-size determinations[33] are an essential part of the analytical examination of powdered materials. Especially in cases where the fine state of subdivision is produced as an aid to chemical reactivity or as a result of chemical treatment, such as precipitation or emulsification, size examinations fall within the scope of chemical analysis. The behavior of a powdered material is often more affected by its fineness than by variations in its chemical composition.

In dealing with powdered materials that lie within the range of testing sieves, microscopical examination is a valuable supplement to the ordinary methods. It reveals the shape of the particles, and hence their actual volume and surface, rather than those of an hypothetical sphere or cube whose diameter is that of the sieve opening. Flaky particles, of large diameter but little volume, or elongated grains of larger volume than their "sieve diameter" would indicate, are likely to introduce serious discrepancies between screen tests and performance, unless recognized microscopically. The character of the grains, whether rough, angular, porous, aggregated, or composite, is further revealed, and in mixtures the different ingredients may be followed through the stages of the grinding, screening, and concentrating operations.

[32] "Handbook of Chemical Microscopy," Vol. I, Chap. XII.

[33] Handbook of Chemical Microscopy, Vol. I, Chap. XIII.

See also the work of Green, Jour. Franklin Inst., **192**, 637 (1921); Perrott and Kinney, Jour. Amer. Ceram. Soc., **6**, 417 (1923); Weigel, Bur. Mines Tech. Paper 296 (1924); Rept. of Comm. E–1, Proc. A. S. T. M., **1930I**, 919–27.

In almost all powdered materials a considerable range of sizes is present, ranging, in the case of ground powders, from the maximum allowed down to ultramicroscopic fineness. The fraction passing through a 325 mesh sieve (opening 44 μ), the finest standard size, contains the particles which contribute almost all of the effectiveness of pigments, fillers, and most other finely divided materials. This fraction cannot be analyzed by sieves, yet it may include particles ranging from the diameter of ordinary fine pigments to those nearly 100 times as coarse.

The size and frequency of sub-sieve particles are best determined microscopically by one of the methods given below. Well dispersed preparations are essential; the particles should lie substantially in one plane, and should be as sharply defined as possible. The mounting medium should be of markedly different refractive index in order to give good contrast, and the lenses used, especially for the measurement of particles $<5\,\mu$ in diameter, should be of the highest quality and resolving power.

Very fine and uniform particles are satisfactorily distributed by "rubbing out" a suspension on a microscope slide, by means of a glass rod held flatwise. The vehicle used should be volatile (xylene or turpentine) and the rubbing should continue until the film of liquid has evaporated. This method is not suitable for coarse particles, which may be crushed, or for non-uniform specimens, which may thereby be segregated. Materials of these latter types should be stirred into a viscous mountant such as Canada balsam or glycerine, and the suspension flattened to a thin layer by pressing beneath a cover glass.

Interpretation of particle-size data in terms of other properties is dependent on the validity of the methods of computation. Any attempt to summarize the dimensional properties of a powdered material by one or two numerical terms is inadequate at best, and should be undertaken only after a thorough study of the methods of expressing results and the significance of the various factors. For example, the expression "**average particle size**" is almost meaningless unless it is clearly understood whether the average has been computed on the basis of weight, surface, or number. Furthermore, an average particle diameter calculated with respect to number is not necessarily applicable to the material the surface properties of which are important, nor can two materials be properly compared except in terms of the same type of "average size." The average size gives no indication as to whether the particles are all of like dimensions, or vary over a wide range; in the latter case averages are of little value.

All particle size determinations, except mere estimations or comparisons (which are very unreliable in the case of non-uniform materials) should be based on **size-frequency measurements**. The number of particles of each size is counted, and serves for the calculation of averages and of uniformity coefficients.

The **methods** of particle-size determination, while not standardized as yet, fall into three classes:

Submicroscopic particles are measured, by counting the number present in a known volume of a suspension of known concentration.[34] The volume of the particles, and their diameter as spheres or cubes, is then computed. The particles are not measured directly, nor is any account taken of non-uniformity.

[34] "Handbook of Chemical Microscopy," Vol. I, pp. 226, 425.

The method gives no information as to size-distribution, and the average particle size obtained is significant only in the case of highly uniform particles; it is suitable only for such material, or in case the fineness is beyond the limit of resolution of the microscope. Fine colloids, "gas black," and the finest zinc oxides are measured by this procedure.

Particles of microscopically measureable dimensions permit size-frequencies to be determined. All the particles in a portion of the sample are counted, and their sizes recorded. A surface- or weight-distribution curve can then be constructed, and averages computed on any desired basis. Such a procedure is of wide application to all types of finely divided materials.[35]

Material of highly non-uniform particle size is often inconvenient to count and measure in all size ranges, and a preliminary fractionation, by sedimentation in liquid, is often advantageous.[36] The fractions may be measured for size-distribution separately, or the average fineness of each may be estimated; the amount of each fraction obtained must of course be taken into account in computing the size-frequency of the original sample.

APPARATUS FOR MICROSCOPICAL ANALYSIS

The apparatus required for microscopical analysis will vary depending on the range of work to be undertaken. A good chemical microscope is the first essential; it should be equipped for crystal studies with polarized light. Magnifications of 200× or less are adequate for a large proportion of the examinations of materials, and for almost all qualitative and quantitative procedures. For particle size determinations on fine particles, 2 mm. or 4 mm. objectives are essential. Hand lenses, or a Greenough binocular microscope, are useful for separating and handling material under moderate magnifications.

If any microscopic measurements are to be made, a calibrated micrometer eyepiece is necessary; for counting of particles, a co-ordinate ruled micrometer is desirable. For systematic movement of the preparation in analysis by counting, a mechanical stage will be required. Counting tallies are a great convenience if large numbers of particles are to be counted. For drawings to scale or areal analyses a drawing camera is essential. A comparison eyepiece is advantageous, if two similar microscopes are available.

The study of opaque objects, such as alloys, will necessitate the use of a vertical illuminator. An artificial light source of suitable intensity and uni-

[35] Perrott and Kinney, loc. cit.
[36] Weigel, loc. cit.

formity, such as a 6 volt ribbon-filament lamp, is an important accessory for examinations at high magnifications, and for photomicrography.

Refractive index determinations require a series of suitable standard liquids covering the range of interest, at intervals of 0.01. A hot stage, with thermometer or thermocouple, must be provided if melting points are to be determined.

A "micro" burner or other device giving a tiny flame about 5 mm. high is a necessity. When gas is available a bunsen burner with "reserve" or "pilot" flame will be found to be most satisfactory (See Fig. 399).

Reagent bottles (best contained in a perforated block), miniature crucibles and holders, distilling and filtering tubes, dropping bottles for liquid reagents, slides, cover-glasses, and the necessary reagents and mounting media are also indispensable to the "micro" laboratory. A collection of authentic samples, for study and comparison, is essential.

The above list of equipment may be somewhat curtailed, but for special purposes and extensive investigations in the general field of chemical microscopy numerous other pieces of apparatus are required; the nature and uses of these are described in various standard works.

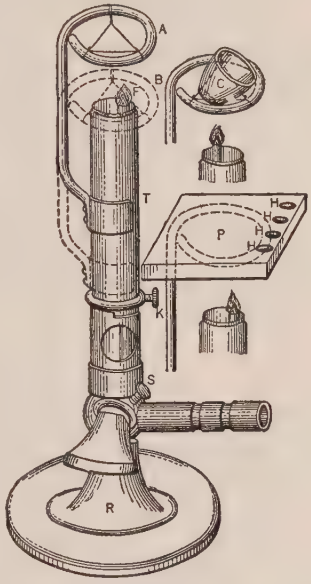


FIG. 399.

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QUANTITATIVE MICROCHEMICAL ANALYSIS[1]

Introduction.—Microchemical analysis may be defined as the determination of very small amounts of constituents when using minute amounts of material. The weight of the sample used for an analysis ranges from 3 to 15 milligrams. Where only small quantities of material are available micromethods must, of necessity, be used, but even where large samples could be used the speed with which a microanalysis can be carried out, without sacrifice of accuracy, has led many men in the fields of both pure and applied chemistry to discard some of the time-consuming macro methods. An analysis can be completed in many cases in less than an hour and very few consume over an hour of the analyst's time. In many cases, and especially in organic analysis, it is necessary to completely oxidize the material in order to obtain accurate results and the advantage here of a small sample over a large one is at once apparent. Anyone who will strictly adhere to the established rules and customs of good analytical technique can acquire within a very short time the skill required in microanalysis. Many chemists, especially in this country, are not using micromethods because they have the false impression that skill can be acquired only after long practice and that the procedures are for the analysis of substances of which only small quantities are available. It is hoped that this impression will be overcome when chemists become familiar with the micromethods and realize that these are authentic and becoming commonly used in all branches of analytical chemistry.

Semimicro differ from micromethods in that a larger sample is used (15–30 mg.) and the weighing may be done on a less sensitive balance to ± 0.05 mg. The apparatus used is essentially the same as in microwork except it may be slightly larger. It is, however, the accuracy of the method which should determine the size of the sample in both methods. In many cases it is the method and not the weighing of the sample which determines the final accuracy. The methods described in the following pages have been chosen from among the great number published, either because these have become standard after many years of use, or are based on principles and methods already well established in analytical chemistry. They are also selected for their convenience and accuracy in routine work. It is not possible, under ordinary laboratory conditions, to weigh to a 0.001 mg. For this reason, sample weights should be chosen that allow the sixth place to vary and not affect the accuracy of the final results. The analyst can, with due care and precaution, use 2 mg. samples and every routine microlaboratory should be prepared and know how to work with such small quantities when such problems arise. It is not felt, however, that microanalysis will fulfill its greatest service to pure or industrial chemistry unless analysts know that the methods are time saving and accurate for routine work. The procedures are, therefore, selected and described with these facts in mind.

[1] By L. T. Hallett, in charge of the department of quantitative microanalysis, Eastman Kodak Research Laboratories, Rochester, N. Y.

The Microlaboratory.—The microlaboratory should have an abundance of north light and be free from direct sunlight. If air conditioning is available it should be used, but it is not essential. The humidity should be around 50%, so that static charges on apparatus are avoided. Microbalances are sensitive to sharp temperature changes so that it is well to try and keep the variation in room temperature within 1° C.

Each man's apparatus (if electric furnaces are used) should be grouped around his microbalance so that unnecessary steps are eliminated. This arrangement is not possible where gas furnaces are employed because of the sharp temperature fluctuation. In such cases, the balance must be located far enough away to avoid this.

The Microchemical Balance.—Within recent years balances have been developed which weigh to 0.001 mg. carrying a maximum load of 20 grams. These balances have without doubt done much towards making microchemistry a practical branch of analytical chemistry.

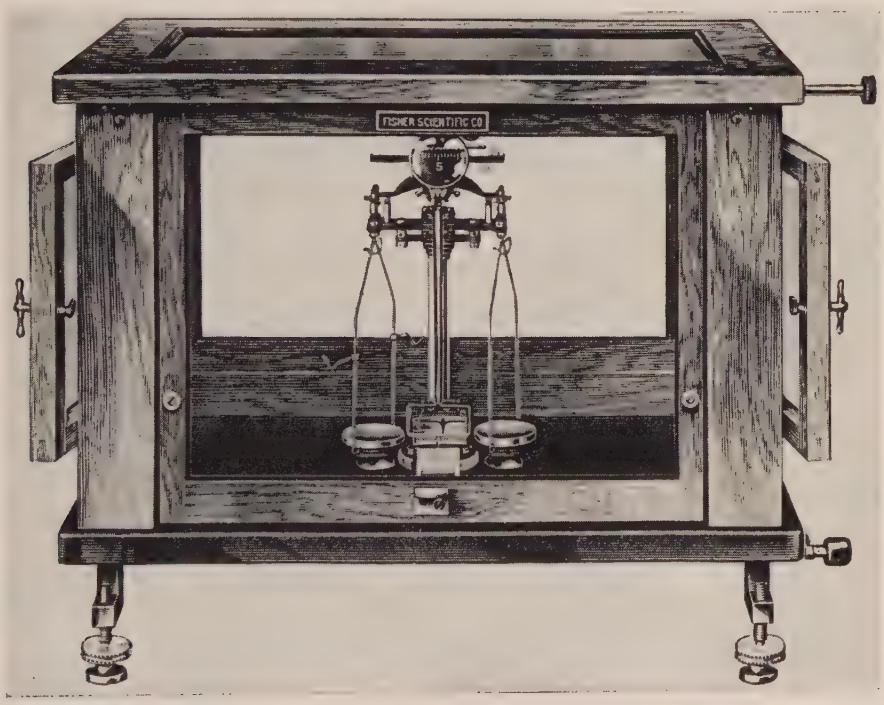

Fig. 400.

The balance, Fig. 400, is best mounted on a concrete slab 3 inches thick which is firmly bracketed against a wall at a height of 3 feet. Strips of lead or rubber are placed between the bracket and the slab in order to absorb vibration. Freedom from minor vibration is not as important as a uniform temperature in the room and absence of air currents. A small table 30 inches high, 12–18

inches wide, and 30 inches long, mounted on casters, is used in front of the balance for holding the notebook, etc. It is made low enough so that it may be shoved under the balance table. The operator by such an arrangement does not lean against or jar the table holding the balance. It is best to place the balance in the same room where the microwork is done so that change in temperature in passing from one room to another is avoided. In order to shield the balance from dust and air currents, it is best placed within a large plate glass balance case 36 inches long, 15 inches wide, and 18 to 24 inches high. A light should not be hung close to the balance but indirect lighting used wherever possible or the light placed far enough away so that the heat given off does not affect the weighing. Side doors are provided through which objects are placed on, and removed from, the pans without raising the front door of the balance. This prevents the breath of the operator from causing air currents and changing the temperature within the balance case. Two hooks are provided on the left-hand stirrup in order that absorption tubes may be more conveniently weighed in a horizontal position.

The beam is shorter than that used in the standard analytical balance and is divided, beginning on the left-hand side, into 100 equal divisions. When a 5 mg. rider is placed in the first notch, the balance, when released, should be in equilibrium. Each division corresponds to 0.1 of a milligram. The displacement of the rider one notch should cause a change of the resting point 10 divisions. By means of the magnifying glass attached to the scale it is possible to estimate one-tenth of a division so that the weighing may be made to an apparent accuracy of 0.001 of a milligram. The change in successive scale readings of a good microchemical balance is very slight and very regular. When the rider is moved the operator should make certain that it falls to the lowest part of the notch and remains in an upright position. A second magnifying glass extends the length of the beam or moves with the rider-arm to enable the operator to see that the rider is properly seated.

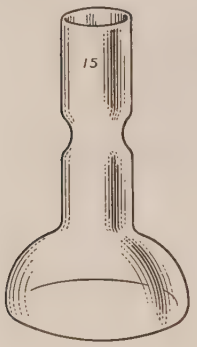

Fig. 401.

All objects which are frequently weighed such as crucibles, weighing bottles, and absorption tubes, should be counterpoised, using a small glass flask, Fig. 401, and glass beads for tare, making a final adjustment by adding an aluminium wire filed the proper amount. For light objects, such as boats, an aluminium wire alone may be used. By this means, most of the weighings may be performed by using only the rider. The 10 mg., two 20 mg., and 50 mg. weights should be calibrated against the rider and filed in order that corrections do not have to be applied. All weights and counterpoises should be kept in the balance-case, and forceps and spatulas should be kept on a glass plate in the large glass balance case. The zero point may be adjusted by means of the small vane at one end of the beam. The sensitivity of the balance should be tested with various loads in the same way that the standard analytical balance is tested, except that the rider is moved 0.1 mg. instead of 1 mg.

The balance should be inspected regularly and the knife-edges and supports kept clean by the use of dry chamois skin.

As far as possible all objects to be weighed should not be touched by the hands because of the moisture and grease always present and also to prevent change in temperature. The object should not be wiped immediately before weighing because of the removal of the film of moisture which will be again absorbed while weighing. The object should be placed on the balance and an approximate weighing made, the final exact reading being taken after the lapse of three minutes. All objects weighed should be kept free from dust, and the hands of the operator should be kept free from dirt and body oil by frequent washing and careful drying. It is the adherence to details, such as these, that makes for success in microanalysis.

A small block of copper, kept in the desiccator, is used to decrease the time for the object to attain the temperature for weighing.

NOTES.—1. In reporting weights they are often expressed in terms of so many (gamma) or (μ gm.) and $\gamma = \mu$ gm. = 0.001 mg.

2. The use of lead shot for filling counterpoise flasks is to be discouraged when the period between weighings is of such length that conditions of temperature and pressure have changed materially. Most of the objects counterpoised are of glass which has a different density than lead. The use of glass beads is, therefore, desirable. A tare of the same size and shape should be used when possible. This cannot be easily done in the case of weighing absorption tubes with some types of balances.

When, for example,[2] five gms. of shot are used to balance a glass vessel, the difference in the volumes of air displaced by the lead and glass is about 1.5 ml. (sp.g. of glass taken as 2.7). The weight of this excess air displaced by the glass vessel will vary 6γ per degree of temperature variation, 23γ per cm. of barometric variation, and about 21γ for the difference between dry and saturated air.

3. In order to simplify weighing in routine work without loss of accuracy, the scale divisions of the microbalance are numbered beginning at the right 0, the midpoint 10, and the extreme left 20. This avoids plus and minus signs. It has also been found that the method of short swings used in macro work can be used with the microbalance. If the total deflection is not over 3 large divisions, then the mean of two successive readings gives the rest point as

$$8.6+11.1=\frac{19.7}{2}=9.8.$$

It is, of course, not necessary for the zero point of the balance to be exactly at the midpoint 10 or that the balance be adjusted to a sensitivity of exactly 10 divisions for 0.1 mg. However, the sensitivity should be kept between 9 and 11 divisions. It is important that the balance maintain a zero point, constant to $\pm$ 0.5 divisions during a series of weighings and a properly working balance will do this if the room temperature is kept within $\pm$ 0.5° C. Where initial and final weighings involve an interval of time the zero point should be recorded in each case so that when a shift in zero point greater than $\pm$ 0.5 divisions (0.005 mg.) takes place the appropriate correction can be made. A typical example of recording and calculating weights is given on page 2464. The zero point is assumed to be constant and a tare is used in weighing the boat.

4. A very good description of the various types of microbalances and their use is given by G. Gorback.[3] Air or magnetic damping is used on some microbalances which helps to speed up weighing. However, a sufficient period (usually 2–3 minutes) for air currents to subside must still be allowed before the final reading is taken. Balances which claim a greater sensitivity than 0.001 mg. are not practical under ordinary laboratory conditions. Such instruments must have every condition rigidly controlled.

[2] Roger J. Williams, Ind. and Eng. Chem., Anal. Ed., **8**, 229 (1936).

[3] Mikrochemie, **20**, 254–337 (1936); also M. Furter, Ibid., **18**, 1–10 (1935).

Example

Sensitivity of balance for 0.1 mg. = 9.2 divisions or 0.1 division = 0.011 mg.

	Beam Reading mg.	Rest Point	
Boat and Sample	5.3	10.9	Difference in rest points 2.3 × sensitivity 0.011 = 0.025 mg. When the rest point of the sample is greater than the rest point of the boat, the weight obtained by multiplying the difference in rest points by the sensitivity is *subtracted* from the difference of the beam readings in order to calculate the weight of sample taken.
Empty boat	0.2	8.6	
Difference	5.1	2.3	
Diff. R.P. 2.3 × 0.011	0.025		
Weight sample	5.075		
Boat and Sample	5.3	6.3	When the rest point of the sample is greater than the rest point of the boat, the weight obtained by multiplying the difference in rest points by the sensitivity is *added* to the difference of the beam readings in order to calculate the weight of sample taken.
Empty boat	0.2	8.6	
Difference	5.1	2.3	
Diff. R.P. 2.3 × 0.011	0.025		
Weight sample	5.125		
Boat and Sample	5.3	8.6	When the rest points are the same, the weight of the sample is found by taking the difference of the beam readings.
Empty boat	0.2	8.6	
Difference	5.1	0.0	
Diff. R.P. 0.0 × 0.011	0.000		
Weight sample	5.100		

Sampling.—If the same care that is used in macro sampling is taken in preparing samples in microwork, the error in microsampling will be no greater than when a larger sample is used. All samples should be finely ground for the reason that a single crystal may weigh as much as 2 mg.

For a mathematical study of the theory and errors in microsampling, the following references are given:[4]

Drying and Weighing Samples.—When a substance requires drying without vacuum, it has been found that a small side-outlet desiccator charged with phosphorus pentoxide or other suitable drying agent, such as "Drierite" or "Dehydrite," and heated internally by a coil of resistance wire inserted through the opening is useful. A vacuum desiccator may be used to hasten drying at room temperature if a high temperature causes decomposition. Substances for analysis should be dried to constant weight. However, in routine work, where a great number of samples must be analyzed each day and speed is a factor, it has been found that for compounds with a high melting point drying overnight at 100° C. in vacuum in the presence of a drying agent is sufficient except in rare cases. A vacuum pistol dryer of the Abderhalden type with electric heating has been found very satisfactory. The design may be

[4] A. Benedetti-Pichler, Z. Anal. Chem., **61**, 305–31 (1922); Baule and Benedetti-Pichler, Z. Anal. Chem., **74**, 442–56 (1928); Joseph Mika, Z. Anal. Chem., **73**, 257–64 (1928).

seen in Fig. 402. The total length is 30 cm. and the diameter of the vacuum drying chamber is 3.5 cm. Ten to fifteen samples, in weighed boats and placed on a glass plate, may be dried at one time and for this reason it is recommended for routine drying. After drying, the samples are placed in the

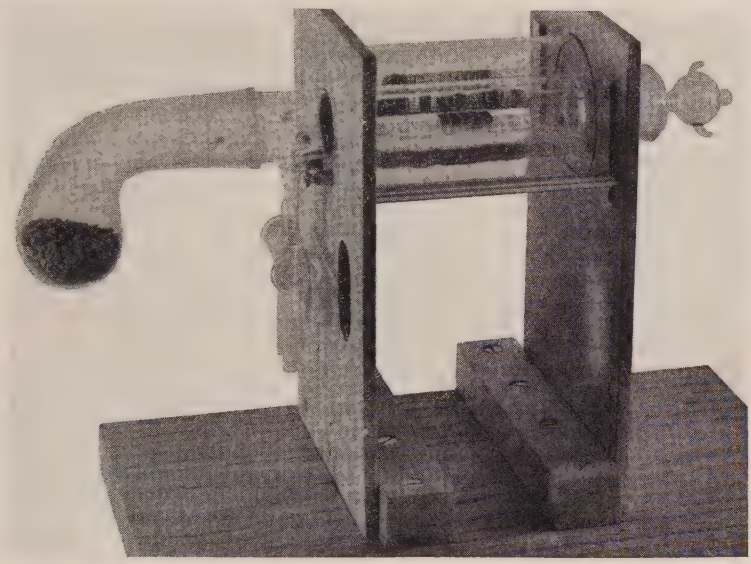

Fig. 402.

small side-outlet desiccator heated to 70° C. Before weighing a sample, it is removed to an unheated desiccator to cool, then placed in the weighing bottle, Fig. 403, and, after standing three minutes on the balance, its final weight is

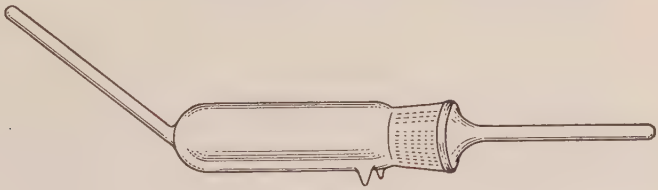

Fig. 403.

taken. The long projections on the weighing bottle are to prevent heating of the bottle by handling.

Drying and Weighing Hygroscopic Substances.—Hygroscopic substances which take up water slowly may be dried in a boat which is quickly placed in the weighing bottle, Fig. 403, previously kept in the balance case. In the case of substances which take up water rapidly and form hydrates, the method of Milner and Sherman [5] is recommended.

[5] Ind. and Eng. Chem., Anal. Ed., **8**, 427 (1936).

A vapor bath, Fig. 404, maintains a constant temperature as in the ordinary Abderhalden. The two-way stopcock can be turned to permit evacuation or the drying of incoming air, the latter entering through a very fine capillary cemented in the plug of the cock and then through the U-tube containing the desiccant. The other end of the tube carries two ground joints, a large one for introducing the plate holding the pig and a small one to hold the brass rod used to open and close the pig while the sample is in the drier. A closed-end mercury manometer is used to seal the small ground joint and to indicate leaks if present when the apparatus is evacuated overnight. The weighing bottle or pig is made without the long projections for handling. A phosphor-bronze spring clip holds the pig firmly in place on an aluminum base with two depressions for

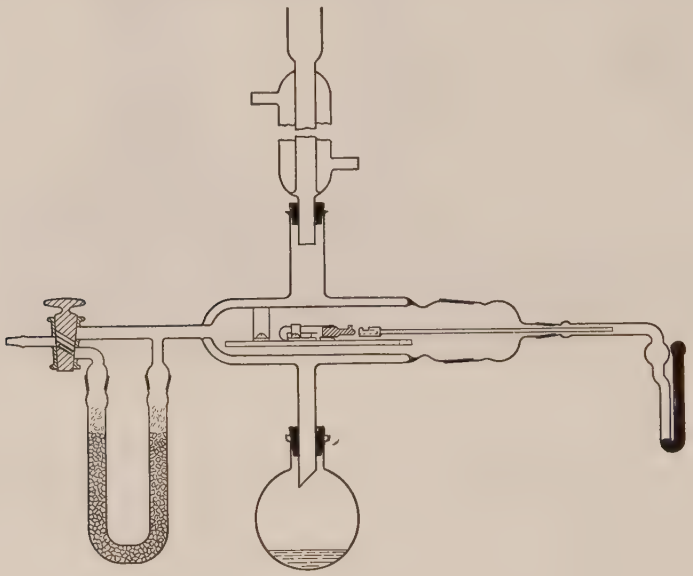

Fig. 404.

the front legs, Fig. 405. The base, whose edges are curved to fit the drier, is held fixed within the drier by another spring clip. The solid glass stopper of the pig has a small handle with projecting knob which is engaged by a brass sleeve comprising a bayonet joint and which enables the stopper to be withdrawn or firmly seated while the pig is in place. Before the sample is weighed out, the pig and empty boat are dried and capped in the apparatus. The sample is weighed and dried and the result recorded. Then the pig is opened and the sample allowed to equilibrate with the moisture in the room. Usually, after 30 to 60 minutes, equilibrium is so nearly approached that any further gain in weight while transferring the sample to the combustion tube is negligible. The pig is then closed and reweighed. The gain in weight upon exposure to air is subtracted from the weight of water found before the percentage of hydrogen is calculated.

The method (see Fig. 402) of heating electrically and having the drying agent attached closer and with a wider opening to the sample is more convenient

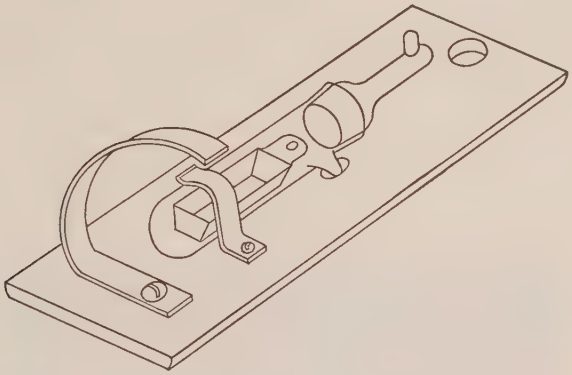

Fig. 405.

than in the Milner and Sherman apparatus. Samples may then be dried at any temperature by simply changing the rheostat setting.

Weighing Liquids.—When the substance is to be oxidized, as in the determination of carbon, hydrogen, sulfur or nitrogen, a capillary tube, Fig. 406 A–B,

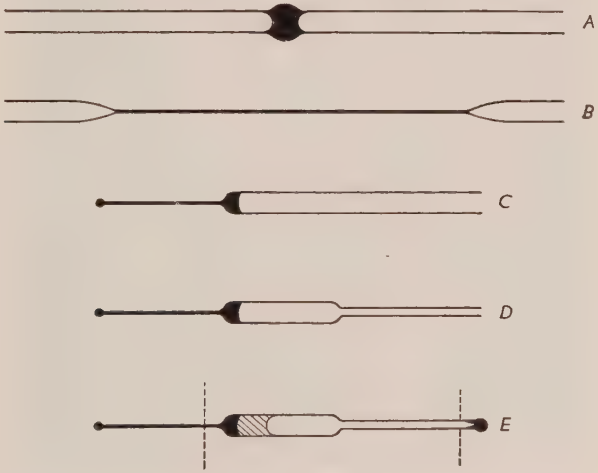

Fig. 406.

is closed and drawn out. A small crystal of potassium chlorate, placed in the capillary, Fig. 406 C, is melted and cooled. A hair capillary is formed by drawing out the open end of the tube, this is broken at a suitable point, Fig. 406 D, and the tube weighed. The tube is then carefully heated to expel the air but not sufficiently to melt the potassium chlorate, the open end dipped into the

liquid to be analyzed and allowed to cool. The excess liquid is carefully removed from the hair capillary by gently heating, after which the tube is sealed and weighed, Fig. 406 E.

The handle and tip are broken off and the tube is placed in the combustion tube on a narrow strip of ignited platinum. It is then quickly placed in position by the use of a platinum or nichrome wire.

For halogen determinations, the potassium chlorate is replaced by ammonium nitrate.

Another method [6] of filling capillary tubes, which is very simple, consists in placing the open end of the capillary in the liquid contained in a small sample bottle. Both are placed in a small filter flask equipped with a rubber stopper and stopcock, Fig. 407. Suction is applied and the flask evacuated, which also

FIG. 407.

evacuates the capillary. This takes only a few seconds. The stopcock is now slowly opened and the difference in pressure between the outside and inside of the capillary forces the liquid into it.

[6] J. Linder, Mikromassanalytische Bestimung des Kohlenstoffs und Wasserstoffs mit Grundlegender Behandlung der Fehlerquellen in der Elementar Analyse Verlag Chemie, Berlin 1935.

Viscous liquids are weighed directly into boats.

Liquids with high vapor pressure,[7] such as acetone, ether, etc., are weighed into a capillary of 1 mm. bore, 30 mm. long with a hair fine capillary end 0.03 to 0.05 mm. bore, 20 to 30 mm. long. The liquid to be sampled is kept cold and the main body of the capillary is warmed, e.g. with warm brass forceps, while dipping in the liquid. It is allowed to cool and the liquid rises in the capillary. Before the capillary has completely cooled, it is lifted out of the liquid with cooled forceps and a small amount of air allowed to enter in order to push the liquid away from the hair fine capillary. The liquid may now be weighed as the hair capillary prevents any weighable quantity of vapor from escaping in ½ hour. The sample is placed in the combustion tube and is surrounded by a cooling mixture while the tube is being swept out. The analysis is then carried out in the regular manner. By using the above method, the vapor slowly escapes into the combustion tube from the open hair capillary as it is carefully heated.

Gases.—Gases, such as those of the hydrocarbon series, may be introduced into a combustion system by the method of Wm. F. Bruce [8] (see page 2480).

Treatment of Rubber Tubing.—All rubber tubing used for connections is placed in a flask with molten vaseline while suction and pressure are alternately applied so that the pores of the tubing are completely filled. The special tubing has an outside diameter of 8 mm. and a bore of 2 mm. Tubing already impregnated can also be purchased from supply houses.

Micro Neubauer Crucible.—The micro Neubauer platinum crucible is used to filter the precipitate in the determination of sulfur and arsenic. The filtering medium is composed of a compressed platinum iridium sponge. The crucible is shown, Fig. 408, attached to a small filtering flask by means of glass tube *G* 10 mm. outside diameter and rubber sleeve *M*.[9] The crucible is prepared for use by washing with the aid of suction with chromic-sulfuric acid mixture and water. The crucible is removed and closed with a lid and lower cap, ignited on a small square of sheet platinum, cooled on a copper block, and weighed.

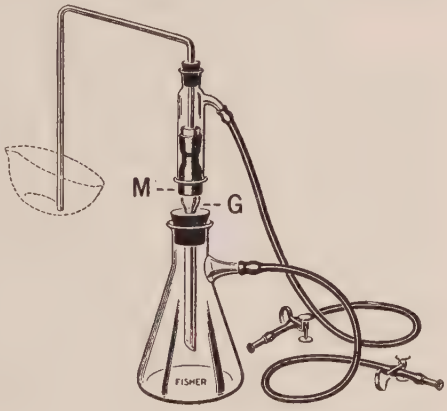

Fig. 408.

The micro Neubauer crucible may be profitably replaced for routine work by porcelain micro filtering crucibles with a filtering medium of unglazed porcelain. In the case of porcelain crucibles, they are ignited in an electric muffle, then, after cooling in the air for 2 to 3 minutes, are placed in a desiccator until they come to room temperature. They are then

[7] G. Pirsch, Ber., **65**, 865 (1932).

[8] Mikrochemie, **18**, 261 (1935).

[9] The arrangement shown provides for the automatic transference of the precipitate to the filter crucible.

weighed at the end of a definite time, say 5 or 10 minutes. If weighings are made the same day, the change in moisture content is not enough to cause serious error when the crucible is ignited and weighed under the same conditions. However, when the analysis is not completed the same day or when the highest accuracy is required, it is best to place the crucibles in weighing bottles.

The Filtering Tube.—The hard glass or quartz filtering tube 11 cm. in length, Fig. 409 A, is first filled with a thin layer of dry Gooch-crucible asbestos, a suspension of asbestos in water added and then the asbestos pad is washed with sulfuric-chromic acid mixture, water, hot nitric acid, water, finally with alcohol and dried at 120–125°.

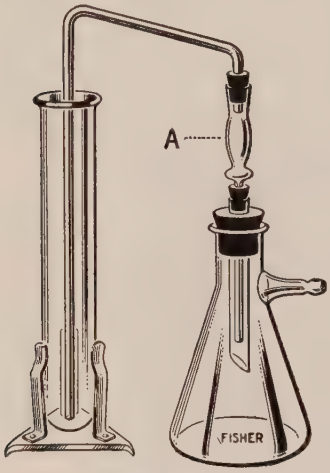

Fig. 409.

A micro Gooch-crucible may be used. The filter tube of Pregl also permits the automatic transference, Fig. 409, of precipitates such as silver halide on to the filtering surface. Hard glass filter tubes with fritted glass filter beds of varying porosity are available and preferred for routine work.

Removal of Traces of Precipitate.—A small feather cemented to the end of a capillary tube or a small rubber policeman is used to remove from beakers and test tubes the last traces of precipitate.

The Immersion Filter.—In the method used by F. Emich [10] the precipitation takes place in a micro beaker and the mother liquor and wash water are removed by suction through an immersion filter or "filterstick." The filter remains in the beaker and both are weighed together; thus, the complete transference of the precipitate to the filter is not required. The method is simple and gives greater accuracy with less skill than when the filter tube of Pregl is used.

The micro beaker has a capacity of 5–10 ml. and is easily fashioned from a pyrex test tube. The immersion filter, Fig. 410, is a capillary glass tube, 2 mm. outside diameter and 5 cm. in length, one end of which is expanded into a funnel or head which may be varied in shape and size but is conveniently 8 mm. in length and 6 mm. in greatest diameter. The total weight of filter and beaker is 6–10 gm.

The filter has a platinum spiral at *P*, Fig. 410, and on this is formed an asbestos mat which is washed and treated in the same way as the Pregl filter tube. The filter and beaker, which have been thoroughly cleaned, are dried in the oven at 105–120° C., cooled in a desiccator without drying agent, and the final weight taken after standing 5 minutes on the balance. Care must be taken to keep the head of the filter up so that the dried asbestos mat will not fall out.

The precipitation is now made in the beaker and after the precipitate has coagulated, the asbestos mat of the filter is moistened with a drop of water and

[10] Stähler: "Handb. d. Arbeitsmethoden," V. 1, p. 680 (Leipzig, 1913). F. Emich, "Mikrochemisches Praktikum," p. 62 (Pub. J. F. Bergmann, 1931).

the filter attached to a suction flask by means of a glass tube and rubber connection. The filter is placed in the beaker with the head just above the coagulated precipitate and the liquid withdrawn into the suction flask, Fig. 411. In

Fig. 410.

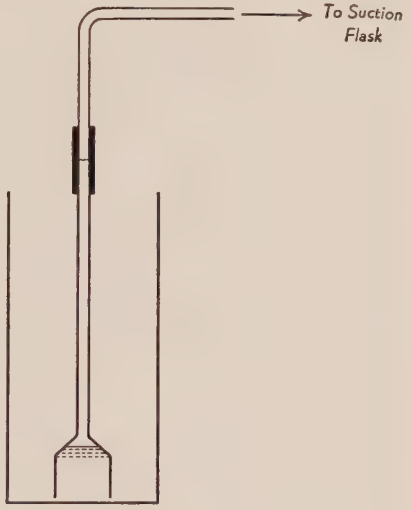

Fig. 411.

the same way the precipitate is washed as prescribed and the wash water removed. The filter is disconnected and remains in the beaker and they are both dried and weighed as before.

If the precipitate must be ignited then the filter and beaker are made of platinum, porcelain or quartz and the filtering medium is platinum sponge, porous porcelain or sintered quartz. A thin porcelain crucible of 10 ml. capacity serves well as a beaker. Where a volume of solution greater than 10 ml. must be handled a microbeaker developed in this laboratory, Fig. 412, with a ground-glass joint, so that the top section may be removed, is useful. The precipitation is carried out as usual and then the filtrate removed by the immersion filter. The bottom section with the filter stick, which has been previously weighed, is now detached, dried, and reweighed with the precipitate. The total weight of the bottom section and filter stick is 8–10 gms.

Fig. 412.

Where ignition is required it is best accomplished in an electric muffle furnace heated to 1100–1200° C. and the beaker with the filter is placed in a covered unglazed porcelain container. After ignition, cooling takes place in the open air for 3 minutes, then in a desiccator with drying agent, and after 25 minutes they are weighed.

In all the microgravimetric determinations to be described the immersion

filter method is applicable, even though it may not be specifically mentioned in the procedure.

Burettes.—For general routine titration work, a 10 ml. burette graduated in 0.05 ml. is suitable. The burette can be read to 0.01 ml. and this is sufficiently accurate for most titrations. Where greater accuracy is required, the graduations should be in 0.01 ml. The graduations should extend around the burette far enough so that parallax can be avoided in taking readings.

Standard Solutions—Titration.—It is good practice to standardize accurately 0.1 N solutions, care being taken that the solutions are maintained at 20° C. 0.01 and 0.02 N solutions are freshly prepared as required by diluting 0.1 N solutions. 0.001 N solutions are not satisfactory as a rule for routine work because of rapid deterioration. Because 0.1 N solutions yield such a large volume on dilution to 0.01 N, much time and labor will be saved if the reagent for the 0.1 N solution is purchased already weighed out and is then diluted to a liter. For most work the accuracy of these reagents is quite sufficient. It is desirable that the solutions be kept in a constant temperature cabinet at 20° C. In summer the use of a constant temperature water jacket on the burette is required for accurate titration, unless air conditioning is available. Most 10 ml. burettes yield too large a drop to obtain an accurate end-point. It is best to wash off the tip of the burette just before commencing the titration, and near the end-point to split the drops and successively wash 0.01–0.02 of a ml. into the flask, until the end-point is reached.

Because of the precision required in micro work all volumetric apparatus should be standardized, preferably by the U. S. Bureau of Standards.

Colorimetry.—It is possible to match colors in the old style colorimetric tubes. It is much better, however, from the standpoint of speed and accuracy to use a microcolorimeter. These are available in 1 ml. capacity. Some special forms have a capacity as low as 0.1 ml.

The use of photoelectric colorimeters [11] is of advantage in routine work where the instrument can be standardized for a particular procedure.

The Heating of Combustion Tubes.—Combustion tubes may be heated with gas or electricity. Gas has the advantage that it will heat the tube up to temperature quickly. Gas burners are readily available in almost every laboratory. However, it has the disadvantage of uneven heating and causing temperature changes in the room as it is turned off and on throughout the day.

Rapid variation in temperature and uneven heating are avoided by the use of electric heating units. Electric heating requires special furnaces which are so designed that if necessary they need not be shut off at the end of each run for cooling of the combustion tube. By this means there is no loss of time from one run to another in getting the furnaces up to temperature.

Apparatus for determinations requiring combustion is usually equipped with gas heat. The author has used both gas and electric heating but favors the latter for routine work. While the methods described for carbon, hydrogen, nitrogen, halogen, and sulfur use electric furnaces, gas furnaces may be substituted. In the case of carbon and hydrogen, the lead dioxide is heated with a mortar filled with cymene which boils around 180° C. Some laboratories use

[11] Withrow, Shrewsbury, and Kraybill, Ind. Eng. Chem., Anal. Ed., **8**, 214–19 (1936); Ralph H. Müller, Ind. Eng. Chem., Anal. Ed., **7**, 223–6 (1935).

electric heating for that section of the tube containing the catalyst or oxidizing agent, but burn the sample with the gas burner.

The electric furnaces, Fig. 414, for the carbon and hydrogen apparatus are constructed by winding nichrome wire on a 6½ and two 3 inch sections of a ½ inch inside diameter porcelain tube. The 3 inch furnace used to heat the lead dioxide is wound with No. 30 wire in three layers separated by alundum cement and asbestos paper. The other two furnaces have two layers of No. 25 wire. The wound cores are hardened by drying at 150° C. The ends of each furnace are made of circles of ⅛″ Transite, 3 inches in diameter. Each furnace is covered with an aluminum or brass shell. Rheostats are used to adjust the furnaces to proper temperature. Ammeters may be put in the circuit to see that the proper amount of current is passing through. Thermocouples may be embedded in each furnace and the temperature may be automatically regulated if the voltage varies. It is best that the lead dioxide furnace be regulated to ±0.2° C. because variation will cause the material to give off or take up water.

The furnaces, Fig. 423, for Dumas nitrogen are of the split type. When the lower half swings down the upper section may then be raised slightly and the furnace pushed away from the combustion tube. The furnace may then be closed and thus kept up to the proper temperature for the next determination. In the drawing the furnace *N* is shown in the position away from the combustion tube, and furnace *O* is shown in the position over the combustion tube. The furnace *N* is provided with two notches, one of which shows at *V*, the other at the same relative position, which fit on the rail *X* so that this furnace may be pushed along the combustion tube.

The furnaces for the halogen-sulfur determination, Fig. 428, are also of the split type, but cannot be shoved back from the combustion tube. The upper half swings open and automatically locks in position. The combustion tube may then be removed and placed on the supports on the front of the apparatus to cool. By pushing the lever at the back the furnaces may be closed and thereby kept up to temperature for the next run.

The construction is shown by the drawings. The furnaces are 3 inches and 7 inches in length and 3¾ inches in diameter. The ends are made of transite. The shell is made of aluminum. Fig. 428 with the top section of the small furnace removed shows the details of construction of the heating elements. The heating element of each half consists of two coils of No. 25 nichrome wire supported on ⅛ inch alundum rods. This in turn is held loosely in place by notched porcelain semicircles which are cemented to the alundum refractory. This refractory consists of a stock alundum tube 1 inch inside diameter, sawed in two. The top and bottom nichrome heating elements are connected in series to binding posts on the transite ends. The heating elements are easily replaced at any time. The furnace temperature is measured by a thermocouple and, if required, suitable resistance is inserted.

For laboratories having a large number of routine organic combustions, the split type electric furnace unit [12] shown in Fig. 413 can be used to advantage. The apparatus is fabricated from aluminum and stainless steel. The drawing shows the small burning furnace, tilted back corresponding to a position away

[12] *Ind. Eng. Chem., Anal. Ed.*, **10**, 110, 111 (1938). This paper gives details of the application of the apparatus to the determination of carbon and hydrogen, nitrogen, sulfur, and halogen.

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from the combustion tube which is not shown, and the large furnace in a position over the combustion tube. A small electric motor with gear reduction drives a screw which moves the sample burning furnace along the combustion tube. When the small furnace is brought in the burning position over the combustion tube, it meshes with the screw, the motor starts and a brush contact, attached to the bottom, passes over a series of insulated metal segments as the furnace moves along. These segments, connected through suitable resistances, automatically vary the speed to give slow initial burning and accelerated burning after the sample has carbonized. The furnace automatically stops when it has reached a predetermined point and the sample has been burned. Any combination of speeds can be obtained by varying the number, positions, and length of the segments. The heating elements are the same as in the hand operated furnace.

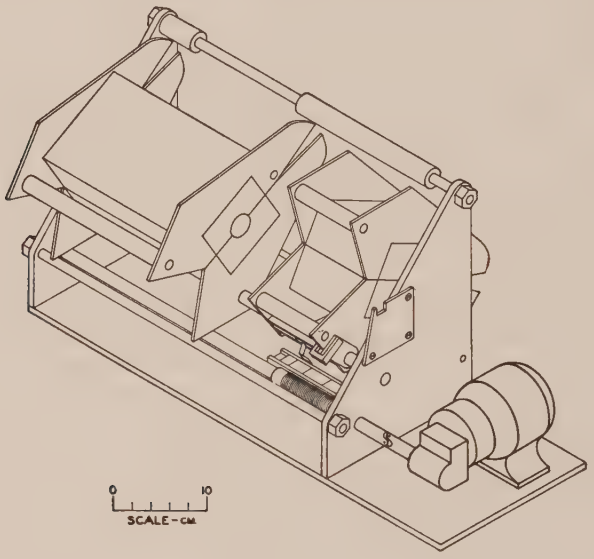

Fig. 413.

The application of this type of burning furnace to the determination of carbon and hydrogen, halogens, and nitrogen increases the number of determinations done per day by about 25%. There is less fatigue for the operator and more time available for weighing, calculating and titrating while the samples are burning.

Many laboratories run combustions only occasionally and a general utility combustion unit for all combustions is desirable. By constructing a three-unit split type which can also be pushed away from the combustion tube, the needs of the small laboratory are met. When running Dumas nitrogen, sulfur, or halogen, the small unit for heating the lead dioxide in the carbon and hydrogen determination may be removed.

Microchemical Equipment.—Practically all apparatus for the procedures here described can be readily obtained from supply houses in the United States.

DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC MATERIAL *

The method [13] described gives a high degree of accuracy together with speed, and can therefore be used to advantage in routine work.

The procedure is similar to the combustion method which is known to all those who have had occasion to determine carbon and hydrogen in organic compounds. The results obtained are as good as, and in many cases better than, those obtained by using the macro method. Results average $\pm 0.1\%$ from theory for compounds containing carbon, hydrogen and oxygen. Those containing sulfur, halogen and nitrogen vary $\pm 0.2\%$ from theory.

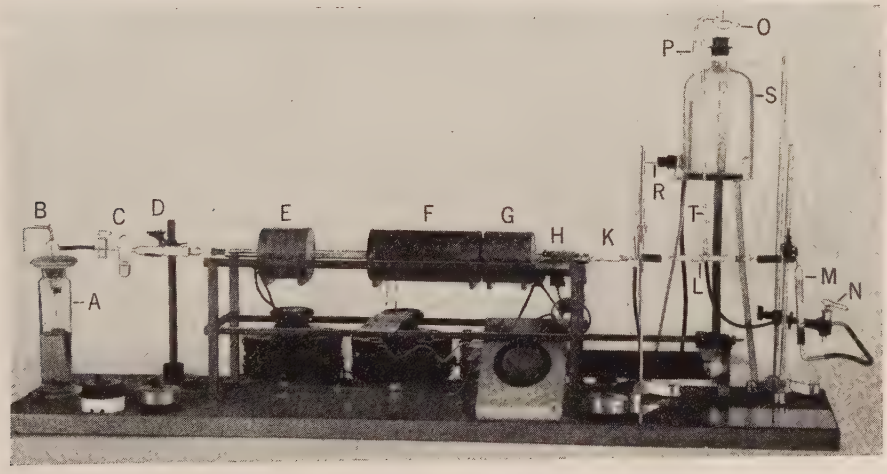

Fig. 414.

Apparatus.—A general view of the apparatus is given in Fig. 414. The pressure regulator *A* is half filled with concentrated sulfuric acid and is then connected at the point *B* by a glass tube with rubber connection to a cylinder of oxygen, preferably made from liquid air. The pressure regulator is attached with a rubber connection to a small bubble counter *C* and drying tube *D*, made of pyrex glass fitted with a ground-glass joint. The bubble counter is partly

* For an automatic combustion apparatus, see p. 2473 and ref. 12.

[13] Kemmerer and Hallett, Ind. Eng. Chem., **19**, 173 (1927).

filled with concentrated sulfuric acid by dipping the end into a beaker of the acid and applying gentle suction on the drying tube *D*. The excess acid is then removed from the end by carefully heating over a burner. The drying tube is charged two-thirds of its length with "Ascarite" (Trade name for sodium hydroxide on asbestos), fine glass wool being placed at both ends (Corning standard wool No. 008); then a layer of phosphorus pentoxide mixed with fine glass wool; and at the end another short layer of glass wool. The ground-glass joint is then heated, the two parts coated with a small amount of glass cement, and after the joint is firmly pressed together it is allowed to cool. A rubber stopper is placed on the tapered capillary end of this joint. The pyrex, or preferably quartz combustion tube, 53 cm. in length and 7 mm. inside diameter, has a capillary opening 1.5 to 2.0 cm. in length. The combustion tube is charged, beginning at the capillary end, with a short wad of ignited asbestos, then silver wool, 1.5 cm.; powdered lead dioxide mixed with asbestos or granular lead dioxide, 4.5 cm.; silver wool, 3 cm.; finely broken copper oxide wire impregnated with lead chromate (by igniting and sprinkling with lead chromate which fuses on the copper oxide), 15 cm.; silver wool, 3 cm. An ignited asbestos wad is placed between each of these charges to prevent shifting. Care must be taken not to pack so tightly as to stop the flow of gas through the combustion tube. Silver removes any halogen and sulfur present, lead dioxide reacts with the oxides of nitrogen, and lead chromate also removes oxides of sulfur. Lead dioxide is heated by the electric furnace *G* to 180° C., copper oxide to 700–750° C. by the furnace *F*, and the third furnace *E* is employed to burn the material in the boat, the temperature of which if necessary may attain 1000° C. The temperatures of the first two furnaces are accurately measured by means of a thermocouple, and as each furnace has a rheostat and a means of reading the current by a small ammeter, it is possible to regulate the temperature accurately. The control of the temperature of the lead dioxide is very important as fluctuations in temperature cause it to give up or absorb water vapor. The furnaces are placed on two rods so that they may be moved along the combustion tube at will. At the point *H* a small electric heater is placed in order to prevent condensation of moisture. The heat applied should be regulated so as not to damage or destroy the rubber connection. The combustion tube when freshly charged is kept at full heat for not less than six hours while a slow stream of oxygen is passed through the tube in order to burn organic matter and free the tube and filling from absorbed gases, such as water vapor.

Absorption Tubes.—Because the oxygen used in the combustion is not swept out with air and since phosphorus pentoxide is used for the absorption of water, the absorption tubes must be capable of being sealed in order to prevent the escape of oxygen or the entrance of moisture during weighing.

The absorption tube, Fig. 415, is made from a 6 mm. pyrex ground-glass joint. The main body of the tube is enlarged until it is 7 cm. in length and 1.3 cm. in diameter with thin walls to keep the weight as small as possible. The mercury bulbs *C* at each of the tubes are identical, the internal diameter being 3–4 mm. The internal diameter at *A* and *B* is 0.2 mm. As an added precaution bulbs 2.5–3.0 mm. are blown between the points *B* and *D* to catch any mercury which might be carried through. The straight part of the tube *D* has an internal diameter of 1 mm. and for a length of 1.5 cm. an external diam-

eter of 3 mm., which fits the special micro tubing used. In Fig. 415, *F* is solid glass to strengthen this part of the tube. The mercury is shown sealing the capillaries. When the tube is rotated 180° and shaken slightly, the mercury falls and the tube is open. The ground-glass joint is sealed with glass cement.

Fig. 415.

The total length of the carbon dioxide absorption tube is about 12 cm. and that of the water absorption tube slightly less. It is very important that these tubes be washed in chromic-sulfuric acid mixture, and then with water, followed by alcohol and finally ether, so that the main body of the tube is clean and also the capillaries on either side of the mercury chamber.

A modified construction for these tubes has been described.[14] The mercury trap and seal are placed within two hollow glass stoppers which are ground to fit the ends of a Pyrex tube 1 cm. in diameter, Fig. 416. The tube is shown

Fig. 416.

unsealed in the figure. When the tube is rotated 180° the mercury drops seal the capillaries.

The water absorption tube *K*, Fig. 414, is charged first with a wad of fine glass wool (Pyrex Standard); then phosphorus pentoxide mixed with a small amount of fine glass wool; and then a wad of glass wool. The end of the tube is then heated and sealed with glass cement. A small drop of mercury is then drawn into each end by means of gentle suction.

The carbon dioxide absorption tube *L* is charged first with a short layer of glass wool; then three-fourths with 20-mesh "Ascarite"; a short layer of fine glass wool; then a short layer of phosphorus pentoxide; and finally a wad of fine glass wool. The tube is then sealed and mercury drawn in.

The ends of the tubes in all cases must be glass to glass in order to minimize the diffusion of gases through the tubing. The charges in both tubes will last for 30 to 40 determinations. The "Ascarite" changes color from a light brown to a grayish white upon absorbing carbon dioxide. A guard tube *M*, filled with phosphorus pentoxide or "Dehydrite," is placed at the end of the carbon dioxide absorption tube and the guard tube is attached to the Mariotte flask. The Mariotte flask or aspirator bottle *S* is used to measure the amount of gas passed through the combustion tube and aids in keeping the system at atmos-

[14] Cornwell, Ind. Eng. Chem., Anal. Ed., 3, 4 (1931).

pheric pressure, and thus minimizes diffusion of gases through the rubber connections.

By means of a three-way stopcock *N* between the flask and guard tube the speed of the oxygen can be regulated. It is also possible by means of stopcock *N* to open this line to the atmosphere before removing the absorption tubes, and thus create an outward pressure which prevents the absorption of moisture and carbon dioxide from the air. By opening stopcock *O* to the air, and attaching tube *P* to a water tap, it is possible to fill the bottle without removal from the stand. Tube *R* runs to the sink and is constricted, or may have a stopcock, so that while the flask is being filled, water will not readily escape.

Procedure.—The furnaces are turned on and also the small heater *H*; the absorption tubes are wiped with a damp cloth, dried, and after unsealing (by rotating 180° and tapping lightly), are attached to the combustion tube. The oxygen is turned on and the pressure in the Mariotte flask regulated so that the gas passes at the rate of 10 ml. per minute, and is allowed to pass while a 3 to 7 mg. sample is being weighed in a cleaned and ignited porcelain or platinum boat, suitable precautions being taken if the substance is hygroscopic or a liquid. The heater *H* is turned off 5 minutes before the absorption tubes are removed. The stopcock *N* on the oxygen line *T* of the Mariotte flask is turned so that the oxygen flows into the air. The guard tube is removed while oxygen continues to flow and then the "Ascarite" tube *L* is removed. The tube is rotated 180° and is tapped lightly causing the mercury to seal the capillaries. The phosphorus pentoxide tube is handled in a similar manner. In removing the tube only the ends and not the main body are touched, and these are carefully wiped each time. It is only necessary to wipe the main body of the absorption tube at the beginning of the day's run to remove accumulated dust.

The phosphorus pentoxide tube is placed on the balance, its approximate weight obtained, and is allowed to stand 10 minutes before the final reading is taken. The other tube is then weighed in the same manner, after remaining 3 minutes in the balance. While the first tube is on the balance the boat containing the weighed sample is placed in the combustion tube by means of platinum-tipped forceps and a clean platinum or nichrome wire. The flow of oxygen now sweeps out any moisture and carbon dioxide which has entered. The absorption tubes are attached, the flow of oxygen is regulated to 5–6 ml. per minute by the stopcock *N*, the combustion furnace is turned on, and the sample is burned by slowly moving the furnace over the boat. The small heating coil at the capillary end of the combustion tube is turned on to prevent the condensation of water vapor. The actual burning of the sample takes about 5–10 minutes and another 20–30 minutes is allowed to sweep out the products of combustion, 100 ml. of oxygen during the first 15–20 minutes, another 200 ml. in 20 minutes. In most cases a total of 200 ml. of oxygen is sufficient. The correct amount should be checked by running standard samples. The absorption tubes are then removed, sealed, and weighed as before.

While these are coming to equilibrium in the balance, the duplicate sample is placed in the tube and after the tubes are weighed and attached, another analysis is made in the same manner. From the weights of carbon dioxide and water the percentage of carbon and of hydrogen in the sample is calculated.

NOTES.—(1) The sample should not be oxidized so rapidly that the gases formed are forced into the tube *D*. A capillary is placed in the tube to help prevent this.

(2) The current of oxygen should be carefully regulated so that the gases formed may pass over the several fillings at such a rate that they are completely oxidized and absorbed.

(3) The system should be tested for leaks by turning off stopcock *N* and observing the bubble counter *C*.

(4) The blank test is very important. This is carried out in exactly the same manner as in an ordinary combustion except that no sample is placed in the boat. If the absorption tubes show an increase of 0.1 mg. or more, the apparatus should be inspected for the following: leaks, excess glycerol on the rubber connections, insufficient time allowed for burning and conditioning a new tube filling, or oxygen containing impurities. Before beginning a series of determinations a standard should be run, preferably containing those elements present in the samples to be analyzed.

(5) The absorption tubes and drying tube *D* are refilled by heating the ground glass joint, which melts the glass cement and allows the tubes to be emptied and refilled.

(6) Because phosphorus pentoxide and " Ascarite " are used, oxygen may be passed through the apparatus at a more rapid rate than that recommended by Pregl. For compounds containing much nitrogen and sulfur the rate should be slower, not more than 5 ml. per minute, so that the oxides of nitrogen and sulfur will be reacted upon by the reagents in the tube.

(7) The absorption tube next to the furnace should always be placed with the ground glass joint away from the furnace to avoid softening of the cement.

(8) The oxygen may contain organic impurities in which case a preheater is used consisting of a combustion chamber filled with platinized asbestos or CuO heated to 650–700° C. by an electric furnace or burner. The gas is usually cooled by passing through a glass coil immersed in water so that it will not decompose the rubber connections. The gas is then passed through " Ascarite " and phosphorus pentoxide before entering the combustion tube. A common type [15] is shown in Fig. 417. Another simpler form made of Pyrex and without a ground-glass joint was designed by White and Wright.[16] " The apparatus is constructed, Fig. 418, from 10 mm. Pyrex tubing, into which two 4 mm. tubes, *AB* and *BC*, are joined by ring seals at *B*. The gas inlet and outlet being attached, the bottom of the tube is sealed off, and, in operation, may be immersed in a beaker of water to cool the burned gases. Into the annulus around *BA* is packed 1.5 cm. lengths of coarse fibre asbestos, and then fluffy platinized asbestos. The top of *BA* is then loosely packed with coarse fibre asbestos and the top of the 10 mm. tube is sealed off. An electrical heating unit surrounds the top of the preheater. It should not fit too tightly and should be closed at the top with a stopper of asbestos paper which can be removed in order that the correct (dull red) temperature may be ascertained."

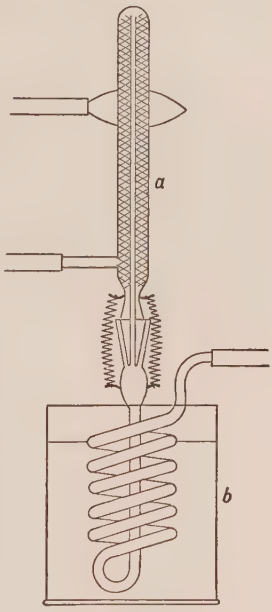

FIG. 417.

(9) Where compounds contain arsenic, antimony, tin, bismuth, or phosphorus, the following procedure [17] is recommended which is a modification of the Falkov and Raiziss procedure.[18] A portion of the copper oxide-lead chromate filling of an ordinary Pregl Universal filled combustion tube is removed and replaced by a 3 cm. cylinder made of 200 mesh platinum wire gauze filled with granulated lead and a 1 cm. plug made of

[15] Niederl and Roth, Ind. Eng. Chem., Anal. Ed., **6**, 273 (1934).
[16] Can. Jour. Res., **14**, Section B, 427 (1936).
[17] F. C. Silbert and W. R. Kirner, Ind. and Eng. Chem., Anal. Ed., **8**, 353–5 (1936).
[18] J. Am. Chem. Soc., **45**, 998–1003 (1923).

platinum wire gauze. The red lead is prepared by igniting Merck's granular lead peroxide in a stream of oxygen in a microcombustion tube in an electric combustion furnace at the normal combustion temperature. To prevent any red lead dust from sifting through the platinum gauze, a thin layer of asbestos lines the entire inner surface of the cylinder, including the ends. This snug fitting cylinder ensures more intimate contact of the combustion gases with the red lead than if the latter is merely placed in a boat as recommended by Falkor and Raiziss. The details of the filling are shown in Fig. 419.

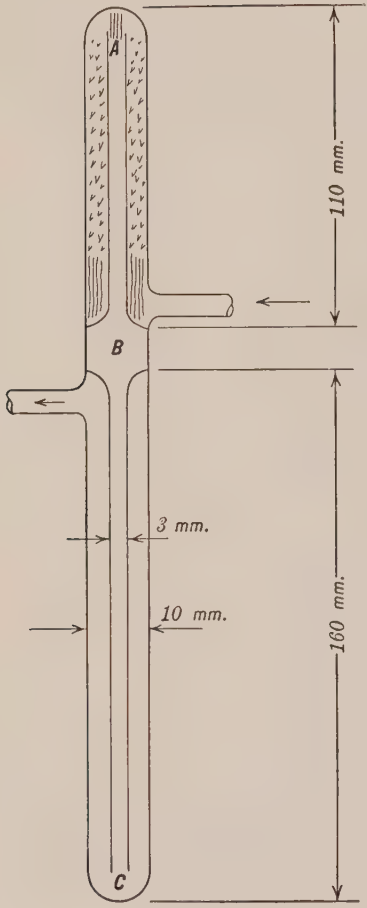

FIG. 418.

(10) Analysis of Coal for Carbon and Hydrogen.

No special technique is required, but the sample must be finely ground (about 100 mesh) in an agate mortar. For accurate analysis, it is necessary, of course, to dry the sample, weigh in a weighing bottle, and then transfer it quickly to the combustion tube before it takes up moisture. Moisture cannot be determined by micro methods because this figure should represent a large mine run sample. The sampling of the coal is, likewise, done in the usual macro way. The final sample which is submitted to the analyst is then taken and prepared for analysis. Kirner [19] gives the following example: 50 gms. of German bituminous coal in fairly large pieces were crudely ground in a mortar, sample *A*. Five grams of sample *A* were pulverized for 5 minutes, sample *B*. Sample *B* did not give concordant results but on taking 1 gram of sample *B* and pulverizing in an agate mortar for 5 minutes, it gave satisfactory checks. Lucas and Grassner [20] take the final 125 gm. sample, grind to 100 mesh, and take 10 mg. of this for a determination.

(11) Solid compounds which are explosive when heated are mixed in the boat with fine copper oxide or some inert material such as ignited finely ground silica.[21]

(12) Where compounds are run which contain carbon, hydrogen and oxygen, the tube filling can be much simplified. Only platinized asbestos, or better, platinum contacts are required to attain complete combustion. This filling is heated by the furnace which heats the lead chromate-copper oxide mixture. Because nitrogen is absent, no lead dioxide is required.

(13) If the apparatus has been standing for a week or so, it is best to burn in the combustion tube a few crystals of sugar or, preferably, a few milligrams of a compound containing the elements present in the compounds to be analyzed. It sometimes happens that the first run is low in hydrogen due to the lead dioxide absorbing moisture. By first burning an organic compound, the water-lead dioxide equilibrium is made constant.

(14) A side inlet combustion tube is often preferred, especially for carbon and hydrogen work. A solid rubber stopper is then used.

(15) Analysis of Gases for Carbon and Hydrogen.

The method essentially consists of measuring the gas accurately in a gas burette,

[19] Ind. Eng. Chem., Anal. Ed., **5**, 363–9 (1933).
[20] Mikrochem., **6**, 116–32 (1928).
[21] M. Furter and J. L'Orange, Mikrochemie, **17**, 38–42 (1935).

mixing it with oxygen, and then passing it into the combustion tube. A special tube with side inlet, Fig. 420, filled with CO_2 absorbent, such as "Ascarite," is placed between the pressure regulator and the drying tube with bubble counter. The measured gas sample, plus an excess of oxygen contained in a gas burette, is attached to the inlet *A* by a tight glass to glass connection of capillary tubing. The apparatus is swept out with air or oxygen. The oxygen from the pressure regulator is cut off. The gas sample

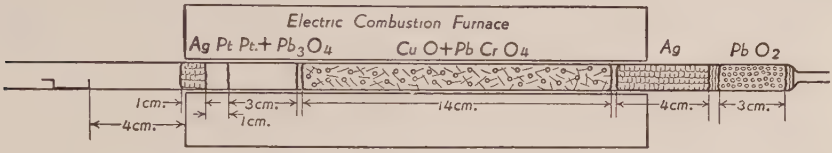

FIG. 419.

mixed with oxygen is now admitted from the gas burette at the same rate as in a regular combustion. When all the gas is out, the burette cock is closed and the method of sweeping out is the same as with the standard procedure.

(16) Many absorption tubes have been designed which can be sealed. Those which have a ground-glass joint, which must be turned and lubricated, may give difficulty due to loss of lubricant when wiped. The use of copper wires in the capillaries of

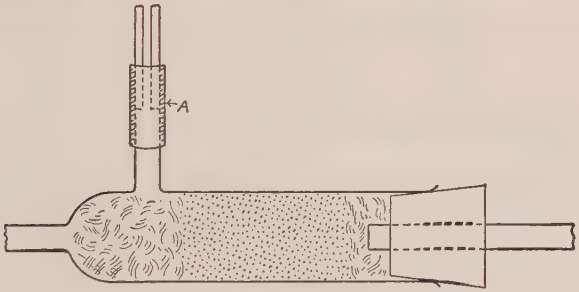

FIG. 420.

the Pregl tube, Fig. 421, to help prevent entrance of moisture and carbon dioxide have been suggested by Boetius [22] and used by Niederl and Roth.[23] The tubes however are filled with air when weighed.

The objection raised to a sealable tube is that changes in temperature and pressure affect the constancy. The author has found, however, that during 45 minutes, which

FIG. 421.

is the time taken to make a carbon and hydrogen determination, it is rare that there is so great a change in pressure as to affect the accuracy of the determination. The temperature of the laboratory does not vary enough to make it a factor. For routine work, a sealable tube which can be weighed while filled with oxygen is much more convenient. The wiping at the end of each run of the main body of the absorption tube has not been

[22] Uber die Fehlerquellen bei mikroanalytischen Bestimmung des Kohlen-und Wasserstoffes nach der methode von Fritz Pregl, p. 27, verlag chemie Berlin 1927.

[23] Ind. Eng. Chem., Anal. Ed., **6**, 272 (1934).

found necessary. References to the different types of sealable absorption tubes are given by A. Friedrich.[24]

(17) The water absorption tube may be filled with a desiccant such as "Anhydrone" (anhydrous magnesium perchlorate) and then finally a ½ inch layer of phosphorous pentoxide, to indicate when the tube must be refilled. Indicating "Drierite" (anhydrous calcium sulfate) may also be used in the water absorption tube. It is impregnated with a cobalt salt which changes to a reddish color on taking up water. It can be regenerated at least 12 times by heating to 235–250° C. for 1 to 2 hours.

(18) Good results have been obtained by replacing a part of the lead chromate-copper oxide mixture with a 4 cm. section of platinum contact foil or a roll of platinum 80 mesh gauze.

(19) The lead dioxide furnace should not be shut off at the end of a series of runs. By always keeping the filling up to temperature the lead dioxide water equilibrium is more readily maintained.

(20) One combustion tube filling will last for 200 determinations. If halogens are frequently run the renewal of the silver wool nearest the boat after 20–30 such determinations is desirable.

(21) Compounds which are salts of alkalies or alkaline earths must be mixed with dry pulverized potassium dichromate in a porcelain boat in order to prevent the formation of carbonates.

DETERMINATION OF CARBONATE CARBON

The carbonate is decomposed with hydrochloric acid and the evolved carbon dioxide absorbed and weighed. The method [25] is accurate when samples containing not less than 1.5–2.0 mg. of carbon dioxide are used; with smaller amounts of carbon dioxide, the error may reach 2%. The values for carbonate carbon vary ±0.3–0.4% from theory.

Apparatus.—The apparatus, Fig. 422, is constructed of Pyrex glass. A rubber stopper is used in the 50 ml. extraction flask *A*, so that flasks may be interchanged. The water condenser is approximately 20 cm. long with the central tube beveled on the lower end *B*, so that it will not be closed by drops of condensed water. The trap *P* containing sulfuric acid, is sealed between the condenser and drying tube *R*, which latter contains the solid drying agents to absorb most of the water before it enters *R*. This trap also indicates the rate of flow of gas through the apparatus. It can be readily emptied by means of the stopcock at the bottom and refilled through the same by applying suction to the apparatus. The drying tube, *R*, 26 cm. long, is made of a 1.7 cm. ground-glass joint, which is sealed with glass cement.

The drying tube is filled with magnesium perchlorate trihydrate, "Dehydrite" or anhydrous magnesium perchlorate, "Anhydrone." This is powdered so that about half passes through a 20-mesh sieve, the two portions being kept separate. The tube is charged first with a wad of fine glass wool, then a 1 cm layer of the coarser "Dehydrite"; fine glass wool; 1 cm. layer of anhydrous

[24] Mikrochemie, **19**, 23–37 (1935).
[25] Kemmerer and Hallett, Ind. Eng. Chem., **19**, 1352 (1927).

copper sulfate to show the presence of water; fine glass wool and alternate 1 cm. layers of coarse and fine "Dehydrite" or "Anhydrone." If sulfites [26] are present the carbonate is decomposed with an excess of potassium dichromate 5% solution, boiled, and toward the end of the procedure, a small amount of dilute sulfuric acid is added.

The acid bulb, *W*, supplied with an Ascarite-filled guard tube, *T*, to prevent absorption of carbon dioxide from the air, is attached to the flask *A* through a

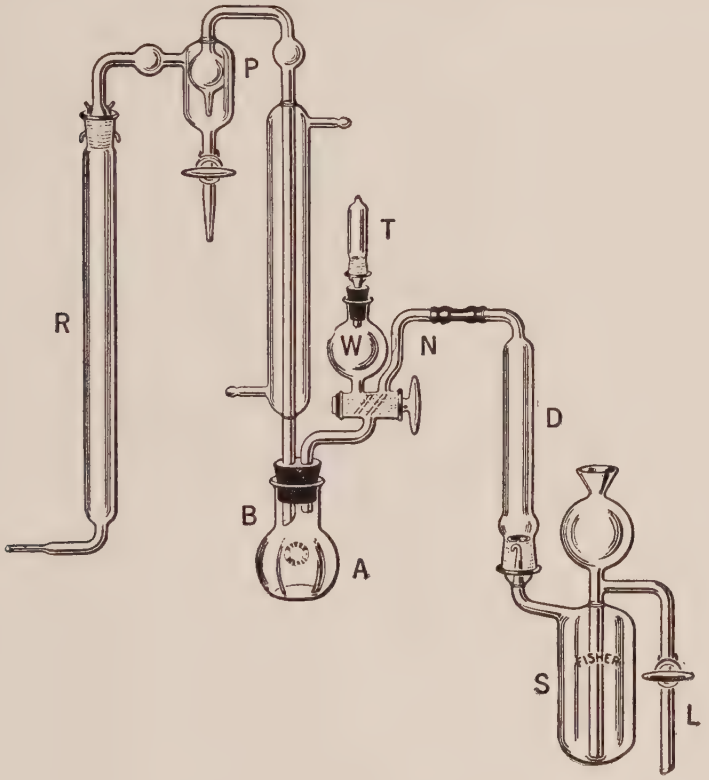

Fig. 422.

three-way stopcock. The air passed through the apparatus to remove carbon dioxide is first drawn through a sulfuric acid trap *S*, which is charged with acid through the funnel and may be emptied by disconnecting it at the rubber connection and blowing out through *L*. The air then passes through the tube *D* which is filled with "Ascarite" to absorb any carbon dioxide present. The constriction *N* retards the diffusion of the carbon dioxide liberated in *A*. The whole apparatus is easily attached to a single ringstand.

[26] E. R. Marle, J. Chem. Soc., **95**, 1491 (1909).

Absorption Tube.—The carbon dioxide absorption tube (see Fig. 415) is charged with "Ascarite" and a short layer of "Dehydrite" or "Anhydrone." For very small amounts of carbon dioxide, 1 mg. or less, it is advisable to use phosphorus pentoxide instead of "Dehydrite" in the drying tube *R* and the absorption tube. The absorption tube is connected to the outlet of *R* and a guard tube charged with drying agent is attached.

Procedure.—When the apparatus is freshly filled, carbon dioxide is passed through and allowed to stand for 2 hours or preferably overnight. The carbon dioxide is then removed by passing air through the apparatus. This operation is repeated whenever the trap *P* is recharged with sulfuric acid.

Five to ten mg. samples are placed on small watch glasses made by cutting the bottom from a test tube, weighed, and transferred along with the watch glass to the flask *A*. The flask is then attached to the apparatus and air drawn through for 10 minutes to remove any carbon dioxide present. Approximately 2 N hydrochloric acid, which has been boiled to remove carbon dioxide, is placed in the bulb *W*. The absorption tube, after careful wiping, is attached to the apparatus and air is drawn through. This fills the tube with dry air similar to that which fills it at the end of the determination.

As the apparatus is under a slight vacuum it is necessary, before removing the the absorption tube, to bring the tube to atmospheric pressure by removing the suction line from the guard tube or by opening a three-way stopcock placed in the suction line beyond the guard tube. One minute should elapse before removing the tube. The tube is then removed, handled and weighed as described under carbon and hydrogen. It is then connected to the apparatus and the guard tube attached. Air is aspirated through the apparatus at the rate of 12 to 14 ml. per minute, and 5 ml. of hydrochloric acid allowed to drop slowly into *A*. When the reaction is complete the current of air is passed for 5 minutes to remove most of the carbon dioxide. The flask *A* is then heated with a micro burner and the solution boiled 2 to 3 minutes to complete the removal of gas. The air current is allowed to continue for 20 minutes or more after the boiling is finished. The suction is then stopped for 1minute and the tube is removed as before, and weighed. While the tube is coming to constant weight on the balance, a second sample, which has been weighed and placed in a clean flask, is attached to the apparatus which is then swept out with air as before. The second determination is carried out exactly as the first. From the weight of carbon dioxide the percentage of carbonate carbon in the sample is calculated.

Notes.—(1) Where oxides of nitrogen are given off [27] powdered lead dioxide mixed with asbestos and heated in a glass tube with an electric furnace to 180° C. must be inserted in the train followed by a tube containing the drying agent. The carbon dioxide absorption tube is now attached as before.

[27] Kenyon and Gray, J. Am. Chem. Soc., **58**, 1422–7 (1936).

NITROGEN BY THE MICRO-DUMAS METHOD *

The micro-Dumas method [28] consists in decomposing the substance by heat in a mixture of fine copper oxide in the presence of carbon dioxide. The carbon dioxide is absorbed in a caustic potash solution and the nitrogen measured in a precision nitrometer. Results average ±0.1% from theory.

Apparatus: *The Carbon Dioxide Generator.*—The Kipp generator shown in Fig. 423 is designed to deliver carbon dioxide of such purity that 100 ml. of

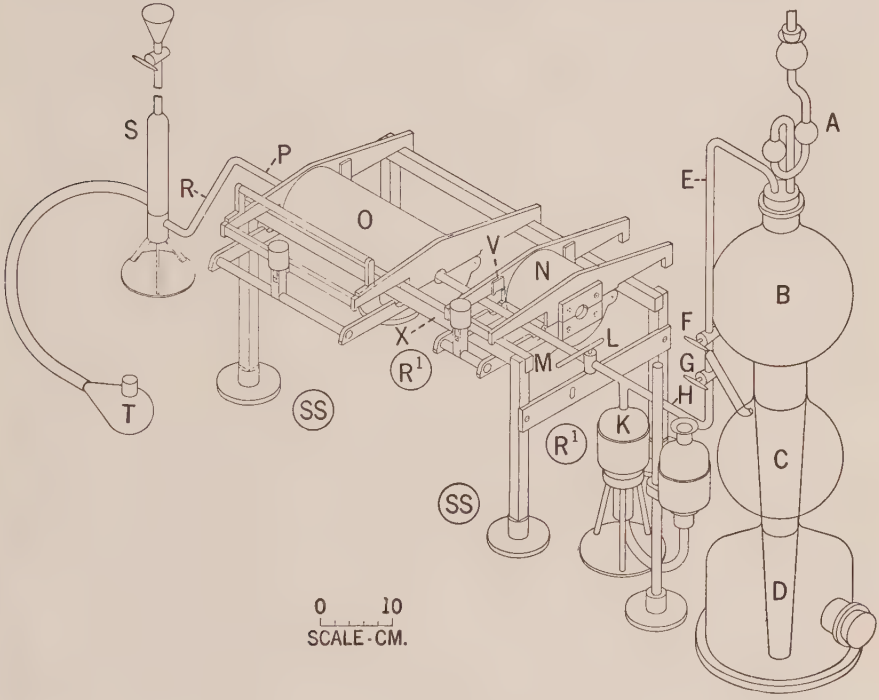

Fig. 423.

gas contain only 0.001 ml. which is not absorbed by a 50% potassium hydroxide solution. In order to keep the acid out of contact with air the upper and middle chambers are connected with glass tubing containing ground glass joints. The acid used is made by mixing equal parts of freshly boiled distilled water and concentrated hydrochloric acid. The marble chips used are etched in dilute hydrochloric acid and then washed with water before they are placed in the generator, in order to remove absorbed gases.

When the generator is assembled and charged, the upper chamber is freed

* For an automatic combustion apparatus, see p. 2473 and ref. 12.

[28] Trautz, Mikrochemie, 9, 300 (1931); Trautz and Niederl, Ind.Eng. Chem., Anal. Ed., 3, 151 (1931).

from air by adding a few lumps of marble, the U tube *A* is put in place, and the upper *B* and middle chamber *C* connected by a glass to glass rubber connection at *E*. Carbon dioxide is allowed to flow from the middle *C* to the upper chamber until there is a positive pressure shown by the mercury in the U tube which seals the upper chamber from the atmosphere. An excess pressure should exist within the upper chamber at all times and the U tube charged with mercury allows the pressure or partial vacuum to be read. A column of mercury 5 cm. high in one arm is sufficient to take care of the variations in pressure. Before an analysis and at other times when necessary, carbon dioxide is passed from the middle to the upper chamber by turning stopcock *F* until gas escapes through the valve. By removing the U tube spent acid may be siphoned off and fresh acid added.

A gasometer *K* containing mercury is placed between the generator and combustion tube in order to measure the volume of carbon dioxide used during a determination. Specially treated and aged rubber tubing previously described (page 2469) is used for glass to glass rubber connections at the points *H*, *P* and *R*. The diameter of the glass tubing at these points is 4 mm. The gasometer is connected at *M* to the combustion tube by a capillary tube, tapered at the end to accommodate the rubber stopper which fits into the combustion tube.

Combustion Tube.—A Supremax or preferably quartz combustion tube, 50 cm. in length, and 7 mm. inside diameter has a 1 to 2 mm. capillary opening 1.5 to 2.0 cm. in length. This tube is the same as that used for the determination of carbon and hydrogen.

The material used to charge the combustion tube is first ignited. The tube is permanently charged, beginning at the capillary end, with a short wad of asbestos, then broken copper oxide wire, 9 cm.; a short wad of asbestos, then 4 cm. of freshly prepared broken copper wire. This is made by passing hydrogen (washed with a solution of potassium permanganate acidified with sulfuric acid) over heated broken copper oxide wire and cooling in a current of hydrogen. A wad of asbestos is added, then 9 cm. of broken copper oxide wire. This is held in place with a wad of asbestos. Before using, the charged tube is preheated in a current of carbon dioxide and then allowed to cool.

Nitrometer.—The precision micronitrometer *S*, Fig. 423, has a capacity of 1.5 ml. and is read to the nearest 0.001 ml. It is charged by adding mercury until it covers the gas inlet. Fifty per cent caustic potash solution made by adding 100 gm. of potassium hydroxide to 100 gm. of water, is then added by the funnel to fill the measuring tube.

Procedure.—A sample which will yield 0.3 to 0.5 ml. of nitrogen is placed in a dry, weighed porcelain boat, dried, and then reweighed. If the material is in large crystals, it should be ground in an agate mortar. Fine freshly ignited copper oxide (prepared by grinding broken copper oxide wire until it passes a 60 mesh sieve) is added to the combustion tube until a layer of 2 cm. is formed, then the boat containing the sample is added, and the tube gently shaken and rotated until the sample is mixed with a fine copper oxide. Another 2 cm. of fine copper oxide is added and then a 4 cm. layer of coarse copper oxide. The end of the tube is wiped with absorbent cotton to remove any fine copper oxide which would prevent the rubber stopper from making a tight fit.

A blank determination using pure cane sugar should be made when the procedure or apparatus is modified, in order to determine the volume of unabsorbable gases which enter during each run. A standard sample should be run before making a series of determinations in order to see that the apparatus is working properly. Liquid materials are weighed in a sealed capillary, the tip broken, and after adding 2 cm. of fine copper oxide, the capillary is dropped into the tube (broken tip first). It is then covered with another 2 cm. of fine copper oxide and finally with 4 cm. of coarse copper oxide.

After introducing the sample, the combustion tube is attached to the apparatus and the air is eliminated by passing through the system about 100 ml. of carbon dioxide, while cold. At the end of this operation, which requires one minute, the nitrometer is attached and small microbubbles should appear in the nitrometer. Bubbles of proper size are recognized by their uncertain rise so that if the gas flow is speeded up the stream of bubbles which are no larger than pin points have a tendency to turn over and go toward the bottom of the nitrometer. If the bubbles are not of micro size, it shows that the air has not been eliminated or that a leak in the system is present. In the next operation, the actual combustion stopcock *L* of the gasometer is closed, both furnaces are brought over the tube, and the combustion tube is heated to red heat (700–750° C.). Care must be taken that furnace *N* does not come too close to the sample and cause premature combustion. After the bubbles have ceased to come over, due to the heating of the tube, any gas which has collected in the nitrometer is now released. The burning of the sample is started by gradually moving furnace *N* nearer and nearer to the furnace *O*. The rate at which the bubbles enter the nitrometer must not exceed 2 bubbles in 3 seconds and this rate is carefully regulated by the proper movement of the furnace *N*.

During the combustion the gasometer is refilled with carbon dioxide. When no more bubbles rise in the nitrometer, the combustion is at an end and the gaseous combustion products are conveyed into the nitrometer by a current of carbon dioxide; stopcock *L* is carefully opened and adjusted to give a rate of one bubble per second for five minutes. The rate of carbon dioxide flow is next increased to three bubbles per second and when the bubbles begin to approach microsize both electric furnaces are opened and pushed away, and the tube allowed to cool. Furnace *N* is shown in position away from the combustion tube while *O* is in the position over the combustion tube. Carbon dioxide is passed through the system until microbubbles of the same size as at the beginning of the run are obtained. The levelling bulb is raised, attached to a holder, and the nitrometer disconnected.

After 15 minutes the readings are taken of the nitrogen volume in the nitrometer with the aid of a magnifying lense to within 0.001 ml. with the potassium hydroxide in the levelling bulb at the height of the nitrometer meniscus, and of its temperature to within 0.1° C. with the bulb of the thermometer touching the wall of the measuring capillary, and of the barometric pressure to within 0.1 mm. The time required from the filling of the combustion tube with the sample and fine copper oxide to the completion of the run is 30 to 45 minutes.

Calculation According to Pregl.—A number of investigators have found that a deduction of 2% from the total volume will take care of any unabsorbable gases liberated from tube filling during the combustion, the vapor pressure of potassium hydroxide and the film of liquid on the side of the nitrometer.

Example.—

Acetanilide sample, mg.		4.950
Volume of nitrogen collected ml. at 29.5° C. and 753.3 mm. pressure		0.471
Calibration correction for burette, ml.	0.001	
2% correction, ml.	0.009	
Total correction		0.010
Net volume of nitrogen to be reduced to standard conditions, ml.		0.461
Nitrogen found, %		10.40
Nitrogen calcd., %		10.37

Calculation According to Niederl and Trautz.[29]—Niederl and Trautz after careful research conclude that more accurate results are obtained by dealing with each correction separately. It has been found that consistently high results are largely due to a more than average amount of unabsorbable gases liberated by the tube filling, or allowed to enter at the time of filling the tube, which amount varies according to individual procedure and set up. These high values are corrected by running a blank before each series of runs and subtracting the blank from the volume reading as illustrated below.

To the volume reading the following corrections are applied:

1. The calibration correction of the nitrometer (from the apparatus certificate).
2. The correction for the air and absorption errors obtained from the blank analysis.
3. 0.5% for the adhesion of the potassium hydroxide solution to the wall; 0.3% for the vapor pressure of the potassium hydroxide solution; 0.3% (approx.) for the temperature reduction of the barometer reading (from 18° to 0° C.) making a total for these three of 1.1%.

The resulting nitrogen volume is reduced to normal conditions (760 mm. and 0° C.) and the percentage of nitrogen calculated.

o-Toluamide sample, mg.		3.475
Volume of nitrogen collected ml. at 24.5° C. and 767 mm. pressure	0.321	
Calibration correction, ml.	0.001	
Air and adsorption correction ml.	0.008	
1.1 per cent correction, ml.	0.003	
Total corrections	0.012	
Net volume nitrogen to be reduced to normal conditions, ml.	0.309	
Nitrogen found, %	10.30	
Nitrogen calcd., %	10.37	

Notes on the Micro-Dumas Method.—(1) The same quantity of fine copper oxide should be used for each determination so that the volume of occluded gases is the same for each run.

(2) Approximately the same volume of carbon dioxide should be used for each determination—when the gasometer is used the correct volume is readily measured out for each run. When the analyst has had experience, the size of the bubbles will determine when enough carbon dioxide has been passed, rather than a fixed volume. However, it will be found that approximately the same amount is used for each determination.

[29] Ind. Eng. Chem., Anal. Ed., **3**, 151 (1931).

(3) If there is a troublesome adherence of the bubbles to the mercury potassium hydroxide interface it may be overcome by the addition of a few drops of mercury previously shaken with ether. The ether is removed with filter paper and the mercury and sludge are washed with potassium hydroxide solution and water, and both mercury and sludge are introduced into the nitrometer through the levelling bulb. The sludge is the essential part of the mixture.

(4) If the potassium hydroxide solution has a tendency to foam in the nitrometer, it is purified by treating with powdered barium hydroxide (5 g. to 200 ml. solution). After shaking, the solution is allowed to stand, and then is filtered.

(5) When standing, the apparatus should be connected to the generator so that a positive pressure of carbon dioxide is maintained, which helps to prevent the absorption of air.

(6) It sometimes happens that due to the needle-shaped crystals of certain organic compounds and to static electricity, the quantitative transference of the sample from a mixing tube to the combustion tube is impossible. By weighing the sample into a small porcelain boat as described, this difficulty is overcome.

(7) A good quality of marble cannot always be obtained in which case the carbon dioxide generator of Poth,[30] Fig. 424, offers advantages and has been successfully used by others.[31] A convenient design is shown in Fig. 424. *A* and *B* are made from 2- and

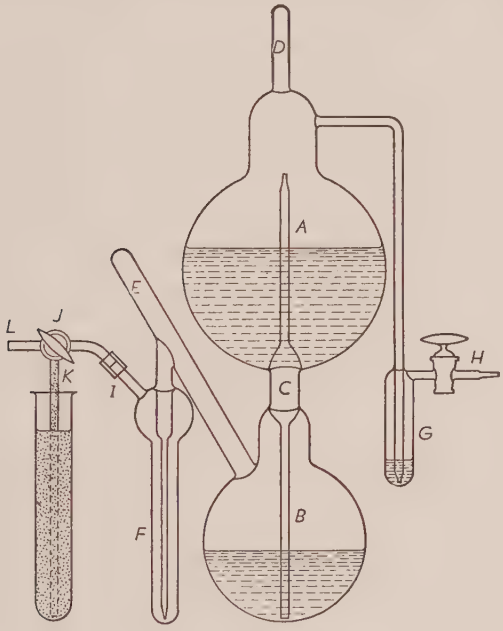

FIG. 424.

1-liter, round-bottomed, Pyrex flasks, respectively. *A* is charged with 500 grams of acid potassium carbonate dissolved in 1200 ml. of water, and *B* with 170 ml. of water followed by 170 ml. of concentrated sulfuric acid. The heat of dilution raises the temperature of the acid almost to the boiling point and thus contributes to the subsequent elimination of contained air. *D* and *E* are sealed, and the desired amount of water is introduced into the bubble counter *G*. Then the T-shaped, three-way stopcock *J* with

[30] Edgar Poth, Ind. Eng. Chem., Anal. Ed., 3, 202 (1931).
[31] Milner and Sherman, Ind. Eng. Chem., Anal. Ed., 8, 331 (1936).

its perpendicular arm *K*, filled with and extending into mercury, is temporarily connected through rubber tubing at *I*, and the entire system is evacuated with an oil pump simultaneously through *H* and *L*. The pumping is continued for about 15 minutes when the appropriate amount of mercury is run into *F*. Both during the pumping and for some time afterward, the bicarbonate solution in *A* will evolve carbon dioxide. Besides being a great help in sweeping out the last traces of dissolved air from the solutions, this property is used in starting off the generator. After closing the T-shaped stopcock, it is disconnected from the suction pump at *L*. The evolution of carbon dioxide in *A* drives the gas into *B* to build up sufficient pressure to force acid into *A* upon evacuation through *H*. If *H* is closed immediately following the introduction of the acid, the gas generated will force more carbon dioxide into *B*. By repeating this procedure, sufficient pressure can be built up in *B* to force the mercury seal *F*. During this process, the T-shaped stopcock is cautiously opened from time to time to ascertain when the pressure in *B* is equal to atmospheric pressure plus the height of the mercury column in *F*. When this is attained, the T-shaped stopcock can be removed, and the generator will deliver a stream of practically pure carbon dioxide whenever *H* is opened. As the apparatus cools, or after it has stood for long periods of time, it may be necessary to apply suction at *H* and again force acid into *A* to reestablish the desired pressure in the system.

Where a supply of dry ice is available, the method of Hershberg and Wellwood [32] provides an excellent source of carbon dioxide and should be used in place of the Kipp generator method if possible. A two-liter vacuum bottle fitted with a mercury U-shaped safety valve and charged with dry ice will generate carbon dioxide for 2–3 weeks. When freshly filled, it should be connected to the apparatus and the carbon dioxide allowed to displace the air in the bottle. This usually requires about 12 hours but, in some cases, it may require a slightly longer period before gas of sufficient purity is obtained.

(8) Ground-glass joints on the combustion tube instead of rubber connections have been used. They are satisfactory but not necessary for accurate work.

(9) Some analysts evacuate the combustion tube after it has been connected for a run in order to eliminate occluded gases. The apparatus requires a three-way stopcock at *L* and *P*, Fig. 423. This procedure cuts down the blank, but where the procedure has been standardized as to the correction to be applied, the evacuation procedure is superfluous when time is a factor.

(10) If the sample is difficult to oxidize, thus giving low results, a small amount, 30 mg., of finely divided potassium perchlorate is sometimes added to facilitate combustion. The excess oxygen is removed by the metallic copper.

(11) Many analysts use a three-way stopcock between the nitrometer and combustion tube. The presence of a stopcock at this point is not required and often develops leaks. The regulation of the flow of carbon dioxide with the stopcock between the combustion tube and the gasometer is much more satisfactory.

(12) The heating of the sample twice, as advocated by Pregl and others, has not been found necessary.

(13) It is best to use two nitrometers so that while one is coming to constant temperature the other can be used for the next run.

(14) The results of Milner and Sherman and E. P. Clark for the vapor pressure of 50% potassium hydroxide show that the subtracting of 0.3% of the volume of gas is too small. While these results are interesting and should be taken into consideration when standardizing a new apparatus, it will be found that for ordinary routine work the subtracting of a fixed percentage will prove more accurate. The blank is essentially a constant for a particular apparatus and its method of operation, and thus will vary according to the individual operator. The following table gives the results of Milner and Sherman [33] together with those of Clark [34] and those from the international critical tables.

[32] Ind. and Eng. Chem., Anal. Ed., **9**, 303 (1937).
[33] Ind. Eng. Chem., Anal. Ed., **8**, 331 (1936).
[34] Jr. Assoc. Off. Agric. Chem., **16**, 575 (1933).

Vapor Pressure of Potassium Hydroxide

Vapor pressure, in mm. of mercury, of solution containing approximately 71.5 grams of potassium hydroxide per 100 grams of water

Temperature ° C.	Fresh Solution	Used Solution	Clark	I.C.T.
15	2.9	3.5	5.5	4.1
20	4.3	5.1	7.0	5.6
25	6.1	7.1	8.9	7.4
30	8.4	9.6	11.4	9.6
35	11.4	12.9	14.0	12.7

(15) Compounds which cannot be analyzed by the Dumas method even with the use of potassium chlorate have been noted by A. Friederich,[35] and Milner and Sherman.[33] No general rule so far has been formulated for those compounds which cannot be analyzed by the Dumas method but there are relatively few such compounds reported.

Hayman and Adler [36] report success in the case of certain pyrimidines which gave low results by mixing about 5 parts by weight of copper acetate to one part of sample and carefully mixing with this about 6–7 grams of fine copper oxide. It was found that decomposition was only complete when a very hot flame was used.

Spies and Harris [37] report a modification of the perchlorate procedure. To overcome the objectionable low decomposition point of the perchlorate, it is decomposed after the combustion of the organic compound while the site of the unburned residue is heated to about 600° C., thereby subjecting the nitrogenous residue to an atmosphere of oxygen at high temperature. The potassium chlorate, 100–125 mg. contained in a porcelain boat, is placed about 40 mm. from the regular filling which contains the sample. A 15 mm. section of copper is added, separated from the regular 40 mm. section of copper by a 3 mm. wad of asbestos. The 15 mm. of copper is removed after each analysis. They report accurate results for compounds which were derivatives of pyrimidine and purine.

(16) For samples that contain only small amounts of nitrogen, less than 5%, and for blank runs, a nitrometer of 0.2 ml. capacity graduated in 0.001 ml. is necessary. Such nitrometers must be made to order.

(17) In routine work the fine copper oxide takes care of the oxidation of the sample so that the main filling of coarse copper oxide is but little reduced. Thus only the fine copper oxide is rejected after each run. A filling normally lasts for several hundred determinations.

(18) It sometimes happens that the liquid seeps from the funnel into the upper part of the nitrometer, thus pushing the column of gas down and preventing a proper reading of the volume. This column of liquid may be pushed back by gently opening the stopcock and raising the levelling bulb above the funnel. With a little practice the liquid can easily be allowed to escape, and when the gas reaches the top of the nitrometer the stopcock is quickly closed before any escapes.

Micro-Dumas Estimation of Nitrogen in Liquids Low in Nitrogen—Milk.[38]—The usual micro Kjeldahl method for estimating nitrogen in small quantities of a liquid such as milk may be satisfactorily replaced by a micro-Dumas process. A small copper boat of approximately 0.25 ml. capacity enclosed in a small thin-walled glass dish covered with a glass plate is accurately weighed, milk added and reweighed. The boat is placed in a small vacuum desiccator and kept at 30–35° C. until the water has evaporated; the boat and its contents are introduced into the combustion tube and covered with fine copper oxide, and the combustion conducted in the standard manner.

[35] "Die Praxis der Quantitativen Organischen Mikroanalyse," Leipzig and Vienna, Franz Deuticke, 1933.

[36] Ind. and Eng. Chem., Anal. Ed., **9**, 197 (1937).

[37] Ind. and Eng. Chem., Anal. Ed., **9**, 304 (1937).

[38] G. Kraemer, J. Prakt. Chem., **97**, 59 (1918).

Nitrogen by Micro-Kjeldahl Method.—There is little that is new in this procedure except the method of ammonia distillation.[39] The method can be used for the determination of nitrogen in organic compounds, soils, leather, feeds, fertilizers, etc. A sample, 3–10 mgm., is weighed in a small watch glass cut from the end of a test tube and is placed into the digestion flask. These micro Kjeldahl flasks are thick walled test tubes with a bulb on the bottom. The time of digestion for any substance is not more than 2 hours, and usually less.

Apparatus.—The apparatus illustrated, Fig. 425, is designed to prevent the condensation of steam and make it possible to attach to a single ringstand. It is built entirely of pyrex glass, eliminating all rubber connections. The steam generator *A* is made from a 500 ml. Kjeldahl flask sealed to the chamber *E* (5.5 cm. wide and 10 cm. high), with openings near the top of *E* to allow the

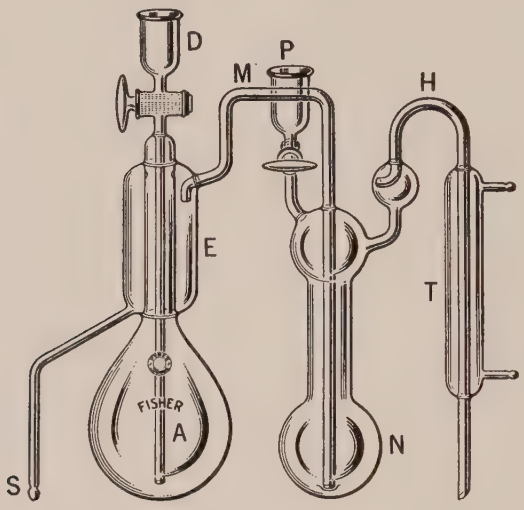

Fig. 425.

steam to pass into *E*, then *M* to the distilling flask *N*. The lower bulb *N* is 6 cm. in diameter and the total height from lower to top of upper bulb is 22 cm. The use of a vacuum jacket around the bulb *N* and partially covering the upper bulb is recommended for routine distillation as it eliminates the burner at this point. The condenser *T* is supplied with running water and burners are placed under *A* and *N*. The steam generated in *A* passes to *N*, liberates and carries ammonia and steam through the tube *H*, and on passing through *T* is condensed and collected in a 50 ml. graduated flask containing 25 ml. of ammonia-free water. The condenser tube is placed below the surface of the liquid and 25 ml. of distillate are collected.

The efficiency of the apparatus is shown by an experiment in which a sample of ammonium chloride containing 0.070 mg. nitrogen was introduced and the

[39] Kemmerer and Hallett, Ind.Eng. Chem., **19**, 1295 (1927).

amount recovered was determined by nesslerization. The average deviation from theory of five determinations was ±0.001 mg.

Procedure.—The weighed sample is placed in the flask and the digestion mixture added. In general this consists of 1 ml. concentrated sulfuric acid, 0.5 g. to 1 g. of potassium sulfate and a small crystal of copper sulfate; 3 drops of alcohol may be added to insure complete decomposition, and to continue time of digestion. For nitro, azo and similar compounds [40] a mixture of 50–100 mg. glucose or dextrose, 1 g. potassium sulfate, a small crystal of copper sulfate and 3 ml. of concentrated sulfuric acid is used. The digestion is continued until the liquid is perfectly clear after which the distillation is performed as described below.

Ammonia-free water is added to *A* through the funnel *D*, and a blank run to make sure that the water or apparatus is free from ammonia. The digested sample and an excess of potassium hydroxide are added to *N* through the funnel *P*. Copper sulfate in the digested sample indicates when an excess of alkali has been added.

The apparatus is prepared for the next sample by removing the burners and allowing the solution in *N* to be drawn into chamber *E* by the partial vacuum caused by the condensation of the steam. A small depression at the bottom of flask *N* facilitates complete removal of the distilled sample. The distillation flask is rinsed by pouring water into *N* through *P*, and heating *A* for a minute. The apparatus is now ready for a second determination. Five minutes are required for a complete distillation.

An aliquot of the distillate, usually one-half, is diluted to 50 ml. in a Nessler tube, nesslerized, and compared with standards treated similarly and at the same temperature.

Results that equal those found by nesslerization are obtained by collecting the distillate in an excess of N/100 sulfuric acid and titrating back with N/100 sodium hydroxide using methyl red as the indicator. If the solution contains carbon dioxide, it must be boiled and cooled just before titrating. Where the sample contains a large percentage of nitrogen, titration is preferable to nesslerization.

NOTES.—(1) Lauro [41] suggested the use of selenium as a catalyst in macro Kjeldahl digestions in place of copper or mercury. It was claimed [42] that more rapid oxidation took place when selenium or selenium oxychloride was used, but from later investigations [43] it would seem that in most cases the time of digestion is not cut down to any great extent. Selenium or selenium oxychloride has a slight advantage over copper sulfate, but no advantage over mercuric oxide. A combination of selenium with mercuric oxide is better than any of these catalysts used singly. The proportions used are 100 parts sodium sulfate ($Na_2SO_4 7H_2O$), 7 parts HgO, 1.5 parts selenium. The above work has been done with macro digestions.

[40] Elek and Sobotka, J. Am. Chem. Soc., **48**, 501 (1926); also Robert A. Harte, Ind. Eng. Chem., Anal. Ed., **7**, 432 (1935).

[41] M. F. Lauro, Ind. Eng. Chem., Anal. Ed., **3**, 401 (1931).

[42] Tennant, Harrell, and Stull, Ind. Eng. Chem., Anal. Ed, **4**, 410 (1932) and C. E. Rich, Cereal Chemistry, **9**, 118 (1932) and R. M. Sandstedt, Cereal Chemistry, **9**, 156 (1932).

[43] R. A. Osborn and A. J. Krasnitz, J. Assoc. Official Agr. Chem., **16**, 110 (1933); Sandstedt, Cereal Chemistry, **9**, 118 (1932), and L. V. Taylor, Jr., Ind. Eng. Chem. Anal. Ed., **5**, 263 (1933).

West and Brandon [44] report that rapid oxidation is obtained by the addition of 0.2% selenium to the micro Kjeldahl digestion mixture. Unlike mercury it does not have to be precipitated before distillation. They give two micro Kjeldahl digestion mixtures. For biological fluids, add 1 ml. of selenium oxychloride to 500 ml. of 1 to 1 sulfuric acid; usually 1 ml. is added to the sample as the digestion mixture. For organic compounds, mix one volume of concentrated sulfuric acid to one volume of a saturated solution of potassium sulfate and add 1 ml. of selenium oxychloride. Use 1 ml. of this mixture for digesting the sample.

(2) The distilling of ammonia into boric acid and titrating directly with mineral acid has been used successfully in several laboratories and was first proposed by Winkler.[45] This eliminates one standard solution. The boric acid retains the ammonia but does not interfere with its titration with acid. A definite quantity of boric acid should be used each time because the color of the indicator varies with the concentration of boric acid. Stover and Sandin [46] used 4 ml. of a 2% solution which is sufficient to retain 0.1 to 21.1 mg. of nitrogen. Distillation is continued until a volume of 50 ml. is obtained. A freshly distilled sample may be titrated directly, but if CO_2 is present the solution must be heated to drive off the carbon dioxide and cooled before titrating. The following indicators may be used: 1. Methyl red (concentration 0.1 gm./100 ml. in 95% alcohol) (use 2 drops). 2. Methyl red and tetrabromphenol blue, made by mixing equal volumes of solutions of the separate indicators. Concentration of methyl red is given above. Tetrabromphenol blue has a concentration of 0.1 gm. in 20 ml. of warm alcohol and diluted to 100 ml. The mixture of methyl red and tetrabromphenol blue changes from green to a gray color when almost at the end-point, and to pale gray-violet with slightly more acid. (Use 2–4 drops.)

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS *

1. According to Pregl.—The method consists in burning the substance in oxygen, passing the products of combustion over red hot platinum contacts and then over a glass spiral moistened with a solution of sodium carbonate containing sodium bisulfite. The sodium carbonate solution absorbs the hydrogen halide and the sodium bisulfite reduces any halogenate or hypohalogenate to sodium halide. Perhydrol is used to oxidize sulfites to sulfates, and silver nitrate to precipitate the halogen.

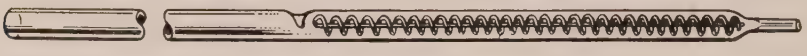

Fig. 426.

Apparatus.—A combustion tube, preferably quartz, Fig. 426, 60 cm. in length and 7 mm. in diameter, is filled to a length of 20 cm. with a hard glass

[44] Ind. Eng. Chem., Anal. Ed., **4**, 314 (1932).
[45] Z. Angew. Chem., **26**, 231 (1913).
[46] Ind. Eng. Chem., Anal. Ed., **3**, 240 (1931).

* For an automatic combustion apparatus, see p. 2473 and ref. 12. For a more convenient absorption apparatus for routine work, see L. Hallett, *Ind. Eng. Chem. Anal. Ed.*, **10**, 111 (1938).

spiral. The spirals have a pitch of 5 mm. and through them runs a glass rod which is sealed to the spiral at each end. The combustion tube is drawn out to a capillary end 1.5–2.0 cm. in length with an opening of 1 mm. A large test tube about 25 mm. in diameter is carefully cleaned with sulfuric chromic acid mixture and water, and charged with a mixture of 2 ml. of pure saturated sodium carbonate solution and three drops of sodium bisulfite solution. This solution is aspirated into that portion of the combustion tube containing the spiral. Then two freshly ignited platinum contacts are introduced. If the contacts become "poisoned" they are etched with hot aqua regia. These contacts are made of platinum foil 0.05 mm. thick. Each contact is 75 mm. in length and is formed in the shape of the letter *Z*. Contacts having greater surface, shaped with six fins (Fig. 427) are on the market and are very satisfactory, or a 15 cm. roll of 80 mesh platinum gauze may be used. The contacts are placed so that they are 8–9 cm. distant from the glass spiral.

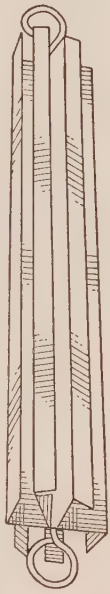

Fig. 427.

Procedure.—5–8 mg. of the substance to be analyzed are weighed in a platinum boat and introduced into the combustion tube. (When iodine is determined gravimetrically 5–10 mg. are used.) Oxygen from a cylinder enters the tube at a rate of 2 bubbles per second, through a capillary tube inserted in a rubber stopper. The platinum contacts are heated to 700–750° C. by the furnace *A*, Fig. 428, and then the material in the boat is slowly burned by furnace *B*. (When iodine is determined it sometimes condenses beyond the heated part and must be driven by heating into the spiral filled portion.) When the combustion is finished, both furnaces are opened and the tube removed to the supports at *C* and *D* on the front of the apparatus where it is allowed to cool in a current of oxygen. The tube and spiral should be washed three times with water free from halogen, the total volume of solution being 30 ml. Two more drops of bisulfite are added and the solution is filtered to remove any suspended matter. In the determination of chlorine and bromine 2 drops of "Perhydrol" are added to the solution, and it is then warmed on the water bath 3–5 minutes. When iodine is present in the solution, heating causes the formation of iodate. This is avoided by adding 4–5 drops of "Perhydrol" and allowing the solution to stand at room temperature for ten minutes. After cooling, 1 ml. of concentrated nitric acid is added and double the quantity of silver nitrate necessary to precipitate the halide. This solution is heated on the water bath 10–15 minutes to coagulate the precipitate, is cooled, and then filtered. The filter tube prepared and dried as previously described under general directions, page 2470, is hung on the balance pan by suspending it on the hook, and weighed. The tube is placed in a filtering flask shown in Fig. 409 and the precipitate is transferred by means of a syphon tube not more than 4 mm. in diameter. The syphon tube is placed just above the precipitate, suction is applied, and the supernatant liquid filtered off. The precipitate is washed by adding a few ml. of nitric acid 1 : 100, then the long arm of the syphon is lowered, and the precipitate transferred to the filter tube by suction. The test tube is rinsed twice,

alternately with dilute nitric acid and alcohol. The syphon is removed, the precipitate washed once with alcohol, the tube wiped and dried at 125° C., cooled, and weighed. The percentage of halogen present in the sample is calculated:

Weighed	Sought	Factor
AgCl	Cl	0.2474
AgBr	Br	0.4255
AgI	I	0.5406

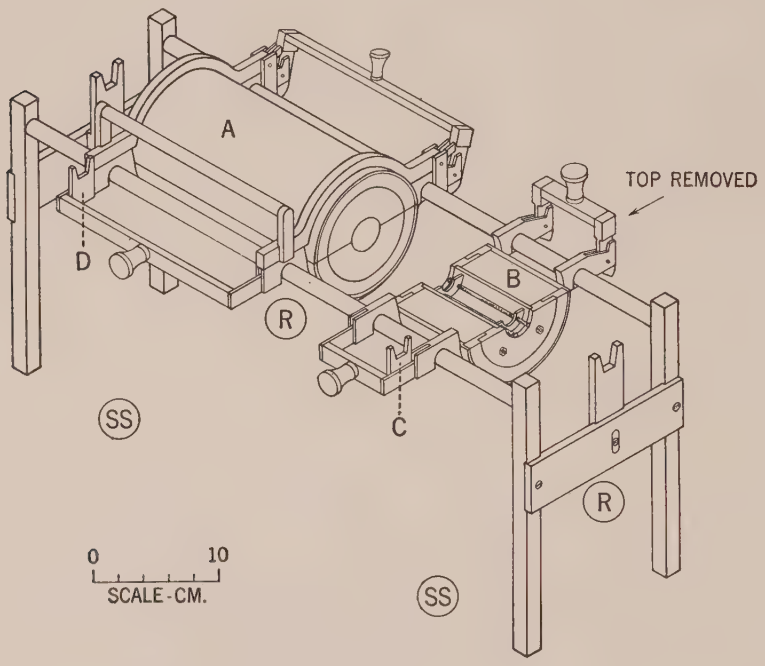

Fig. 428.

Notes.—(1) When substances contain halogen free from sulfur and other elements which combine with metallic silver, the simple method of Dennstedt [47] is often used. The combustion tube without a bead filling is charged first with a platinum boat containing the weighed sample, then two platinum contacts and finally a boat containing a known weight of molecular silver. The contacts are heated to redness and the molecular silver to a temperature of 500–600° C. The sample is slowly burned in a current of oxygen and the products of combustion passed over the platinum contacts, the halogen being absorbed by the metallic silver. The percentage of halogen in the sample is calculated from the increase in weight of the boat containing the silver.

(2) Burning the organic material in a platinum lined micro Parr bomb has been done successfully.[48] A stainless steel bomb is not satisfactory due to corrosion and subsequent erratic results. Beamish [49] in a macro procedure reports that a nickel bomb gives good

[47] C. Funk and Kon, J. Am. Chem. Soc., **48**, 1667 (1926).
[48] Elek and Hill, ibid., **55**, 2550–4 (1933).
[49] Ind. Eng. Chem., Anal. Ed., **6**, 352 (1934).

results even with prolonged heating with bromine compounds, but a stainless steel bomb gives low results under such conditions. The explosion mixture consists of 1.5 gm. of pure sodium peroxide, 300 mg. of a mixture of potassium nitrate and sugar in a ratio of 3 : 1. The lid is clamped on, the mixture well shaken, and exploded by heating the bomb with a small flame. The fusion is dissolved in 1 : 1 nitric acid and filtered, and the halogen determined gravimetrically as silver halide.

(3) Occasionally, a compound will be found which will give low results by the combustion method due to incomplete burning. In such a case the micro Carius method should be used which is, of course, the same as the macroprocedure except for the quantities of material used.

A tube closed at one end 20 cm. long, bore 8 mm., wall 2 mm., is charged with approximately 0.5 ml. fuming nitric acid, 15–25 mg. of silver nitrate, and the sample, which is contained in a capillary if a liquid, or in a glass capsule, if a solid. The tube is sealed, placed in a bomb furnace, and heated at 300° C. for 5–8 hours, cooled (usually overnight), and then after carefully breaking the tube, the silver halide is washed on to a filter, dried, and weighed.

The Volumetric Determination of Iodine.—The method [50] described, is both rapid and accurate. It is recommended in place of the gravimetric procedure for routine work. With samples containing 2–3 mg. iodine, the results vary $\pm 0.1\%$ from theory.

Reagents.—N/50 sodium thiosulfate (made by diluting N/10 thiosulfate with freshly boiled out distilled water).

Normal sulfuric acid solution.
5% solution phenol (quinone-free).
Saturated bromine water.
Potassium iodide (iodate-free).
Starch indicator solution.
Methyl orange indicator solution.

Procedure.—A sample containing 2–3 mg. iodine is burned in oxygen as previously described on page 2494 except that no bisulfite is added to the sodium carbonate solution.

After combustion, the sodium carbonate solution containing the absorbed iodine is washed into a 125 ml. Erlenmeyer flask, neutralized (indicator-methyl orange) with normal H_2SO_4 and 0.1 ml. of acid added in excess. The total volume of solution should not exceed 50 ml. One ml. of saturated bromine-water is added, the solution is shaken and allowed to stand 3 minutes. The excess bromine is removed by the addition of 1 ml. of 5% phenol solution. After shaking and allowing it to stand for 3–5 minutes, solid potassium iodide (Approx. 0.5 gms.) is added in excess, and the liberated iodine titrated with thiosulfate. The iodine present in the original sample is equal to one-sixth of that which is titrated.

Weight of sample	9.997
ml. of N/50 thiosulfate	7.55
One-sixth	1.258
1 ml. 0.02 N thiosulfate	2.538 mg. iodine
Weight iodine in sample	1.258×2.538
Percentage of iodine in sample	$\frac{1.258 \times 2.538 \times 100}{9.997} = 31.94$

[50] Joseph L. Goldberg, Michrochemie, **14**, 161 (1934).

NOTES.—(1) The volume of excess acid (0.1 ml.) added to the bromine solution may be exceeded by 0.1 to 0.2 ml. but more than this is inadvisable.

(2) The phenol should not be added dropwise but in one portion. The dropwise addition of phenol often yields a turbid solution consisting of tri-bromophenol and tri-bromophenol bromide. The latter compound liberates iodine from KI and thus high results are obtained.

(3) The distilled water used should be freshly boiled to remove oxygen.

(4) For micro work, N/100 thiosulfate is often recommended, but at this dilution rapid deterioration of the solution takes place and the time lost in frequent restandardization makes its use in routine work unsatisfactory. N/50 thiosulfate has a constant titer for at least one week. For routine work it is best to make up every week the required amount of thiosulfate by diluting the N/10 solution. The addition of 1% of amyl alcohol helps to prevent the deterioration of thiosulfate solutions.[51] Another method used is by adjusting the pH between 9–9.5 by the addition of borax (3.8 gm. per liter of thiosulfate solution). It is recommended that one of these two methods be used for preserving the N/10 solution.

Volumetric Determination of Chlorine and Bromine.—A micro Volhard method can be used with satisfactory results.

Solutions.

0.02 N silver nitrate.

0.01 N ammonium thiocyanate.

Indicator—saturated solution of ferric alum.

Solution of sodium sulfite.

Concentrated nitric acid (freed from oxides of oxygen by bubbling air through the solution).

Procedure.—The sample containing 1 to 3 mg. of halogen is burned in a combustion tube with oxygen, and the halogen absorbed in sodium carbonate or alkaline hydroxide as previously described. The combustion products are washed into a 50 ml. centrifuge tube in the case of chlorine and into a 125 ml. Erlenmeyer in the case of bromine. The total volume should not exceed 30 to 40 ml. Three drops of sodium sulfite are added and then nitric acid until there is 1 ml. in excess. The presence of sulfur dioxide changes any halogenate to halide. The addition of sulfur dioxide is not necessary if the halogens are in the halide form. An excess of silver nitrate is now added, usually 3 to 5 ml. and in the case of the chloride the precipitated silver chloride is centrifuged off and the excess of silver nitrate is titrated with ammonium thiocyanate, using 1 ml. of indicator solution until a reddish-brown color appears and remains for 3–5 minutes.

NOTES.—(1) It is best to check the end-point by adding another 0.1 ml. of silver nitrate and then titrating again to the appearance of the faint red color.

(2) If the silver chloride is left in the solution, it produces a fading end-point, so it must be removed before titrating. The presence of silver bromide or iodide does not interfere with the titration so they need not be removed. The use of ether,[52] nitrobenzene,[53] benzyl alcohol,[54] toluene,[55] has been suggested for titrating without filtering off the silver chloride. These organic compounds have the effect of coagulating the silver chloride in large particles so that relatively little surface is exposed to cause fading

[51] Mayr and Kerschbaum, Z. anal. Chem., **73**, 321 (1928).
[52] P. B. Rethberg, Biochem. J., **20**, 483–5 (1926).
[53] Caldwell and Moyer, Ind. Eng. Chem., Anal. Ed., **7**, 38–9 (1935).
[54] W. Kimura, J. Soc. Chem. Inc., Japan, **37**, suppl. binding 590–1 (1934).
[55] Vaille and Hauteville, J. Pharm. Chim., **22**, 61–7 (1935).

of the end-point. However, it is best to filter or centrifuge off the precipitate for accurate work.

(3) The presence of sulfur dioxide in the solution also tends to produce a fading end-point and should be removed by heating.

Titrating Halogens Using Adsorption Indicators.—Chloride, bromide, or iodide may be titrated directly with silver nitrate using dichlorofluorescein. For micro work the halide solution must be neutral. This may be adjusted by adding acid or alkali until the characteristic green fluorescence of the indicator appears. Near the end-point a brownish tinge appears; at the end-point the precipitate assumes a reddish-orange color. As the precipitate is very finely divided in dilute solution, the solution itself takes on this color.

NOTES.—(1) The Volhard method for bromide is satisfactory because the precipitate of silver bromide need not be removed, and the acid concentration is not critical. When titrating, using dichlorofluorescein, the solution must be carefully neutralized; thus, time is not saved by using this method for bromine. With chlorine, where centrifuging is required, the use of the dichlorofluorescein titration may save some time. However, the end-point is not strikingly sharp with 0.01 N silver nitrate. Bullock and Kirk [56] found the only way to use the method was by adding an equal volume of acetone to the solution which sharpened the end-point. They also suggest titrating in a partially darkened room by the light of a daylight lamp placed at the side of the observer. A black background is preferred to a white one. Back titrating with standard 0.01 N chloride is possible so that the end-point may be checked. This procedure is also suggested for dilute solutions by Kolthoff, Lauer, and Sunde [57] but the reverse titration must be made immediately, as the indicator reacts slowly if allowed to stand. The correct amount of indicator is 2–4 drops of 0.1% per 50 ml. of solution. If smaller volumes are used, it is better to employ a concentration of 0.01%, 2 drops being sufficient for 4–5 ml. Under the best conditions, the titration error is 0.5 to 1%.

Calculation.—Using 0.020 N silver nitrate.

$$\text{Percentage bromine} = \frac{1.598 \times \text{ml. silver nitrate} \times 100,}{\text{Wt. of sample}}$$

$$\text{Percentage chlorine} = \frac{0.70914 \times \text{ml. silver nitrate} \times 100.}{\text{Wt. of sample}}$$

THE MICRODETERMINATION OF PHOSPHORUS IN ORGANIC SUBSTANCES

Preparation of Solutions: [58] 1. ***Sulfate-Molybdate Reagent.***—50 gm. of ammonium sulfate are dissolved in 500 ml. of nitric acid (sp.gr. 1.36) in a liter flask. 150 gm. of powdered ammonium molybdate are treated with 400 ml. of boiling water in a porcelain dish and stirred until solution is complete. The solution is rinsed into a flask with a little water, cooled to the temperature of

[56] Ind. Eng. Chem., Anal. Ed., **7**, 178–180 (1935).
[57] J. Amer. Chem. Soc., **51**, 3273 (1929).
[58] Neubauer and Lücker, Z. Anal. Chem., **51**, 161–175 (1912).

the room, and poured in a thin stream with stirring into the nitric acid solution of ammonium sulfate. The resultant liquid is diluted to 1 liter, allowed to stand for two days, filtered and kept in a well-stoppered bottle of brown glass in a dark, cool place.

2. *Nitric Acid Containing Sulfuric Acid.*—30 ml. of sulfuric acid (sp.gr. 1.84) are poured into 1 liter of nitric acid (sp.gr. 1.19 to 1.21). The latter acid is obtained by mixing 357 ml. of nitric acid (sp.gr. 1.40) with 500 ml. of water.

3. *A 2% Aqueous Solution of Pure Ammonium Nitrate.*—The solution is acidified with a few drops of nitric acid.

Methods of Oxidizing the Organic Material.—I. According to H. Lieb: The material, 2 to 5 mg., is weighed into a small platinum boat. An excess of finely powdered pure calcined sodium carbonate and sodium nitrate mixed in equal portions is added, the whole is mixed with a short looped platinum wire which is finally laid on the boat, and then carefully covered with the oxidizing mixture. The boat is placed in a pyrex combustion tube about 15 cm. long, one end of which is drawn out to a capillary and bent upwards at right angles. The material is burned in a slow stream of oxygen. As soon as the reaction is finished the boat is heated for some minutes to the full temperature of a Bunsen burner and is then allowed to cool in a stream of oxygen. The material in the boat is then boiled out with dilute nitric acid in a small test tube and poured through a filter into a precipitation vessel which consists of a large thick walled test tube which has previously been washed in sulfuric-chromic acid mixture. If any of the melt has passed into the combustion tube during the reaction this is washed out with dilute nitric acid. To the clear filtrate, 2 ml. of nitric acid containing sulfuric acid are added, and also water if necessary to dilute the total volume to 15 ml.

II. According to H. Lieb and O. Wintersteiner:[59] The following method requires less attention and is simpler than the other, and can be used also to determine arsenic as well. It is reliable in most cases.[60] The sample, 3–6 mg., is digested in a micro Kjeldahl flask with 0.5 ml. of concentrated sulfuric acid and 0.5 ml. of perhydrol until fumes of sulfur trioxide are evolved, cooled, a few drops of perhydrol added and the evaporation is repeated until a clear solution is obtained. To this are added 2 ml. of nitric acid containing sulfuric acid, and water if necessary to make a total volume of 15 ml.

NOTE.—(1) Elek and Hill [61] employ a Parr microbomb using sodium peroxide to destroy the organic matter.

Treatment with Molybdate of Solution Obtained Above.—According to H. Lieb: The liquid, 15 ml., is warmed on the boiling water bath. The hot solution is well shaken, 15 ml. of the sulfate-molybdate reagent added. The vessel then is allowed to stand for three minutes, and again shaken for half a minute. The precipitate is allowed to settle for 30–60 minutes, and filtered with the aid of suction. The filter tube, or filter crucible, is washed with water, hot dilute nitric acid, and again with water, finally displacing the water by alcohol and ether or by acetone. The filter tube is then wiped with a dry

[59] Mikrochemie, **2**, 78 (1924).

[60] A. Elek, J. Am. Chem. Soc., **50**, 1213 (1928), reports a low result when thymus neuclic acid was analyzed by this method.

[61] J. Am. Chem. Soc., **55**, 3479 (1933).

chamois leather, and left for at least half an hour in an evacuated desiccator—*containing no drying agent.* It is removed from the desiccator immediately before use, placed on the balance, and the time carefully noted which has elapsed between removal from the desiccator and the final weighing, which may conveniently be 5 minutes. These conditions must be exactly repeated when the precipitate is weighed.

The precipitate is drawn into the filter tube by means of the same automatic arrangement that is used for the silver halide precipitate, page 2470. After the supernatant liquid has been syphoned from the precipitate it is washed in the test tube with 2% ammonium nitrate solution, and afterwards transferred to the filter; in order to remove the last traces of precipitate from the walls of the precipitating vessel, 95% alcohol and ammonium nitrate solution are used alternately. The tube is finally filled once with alcohol, and then twice with ether or acetone. After drying half an hour in vacuo the tube is weighed under exactly the same conditions as those of the initial weighing. The factors are:

Phosphorus pentoxide	0.33260
Phosphoric acid	0.03326
Phosphorus	0.014524

Volumetric Method.[62]—Instead of weighing the yellow precipitate it may be transferred to the original beaker and approximately twice the amount of N/50 sodium hydroxide necessary for dissolving the precipitate added, and the solution heated to boiling for 5 minutes to drive off the ammonia formed when the caustic is added. The volume of solution should be reduced to 15–25 ml. To the solution after cooling, 5 drops of ½% phenolphthalein indicator is added and 3 to 5 ml. of N/50 hydrochloric acid in excess. The solution is boiled for ten to fifteen seconds, cooled and titrated back with N/50 sodium hydroxide. From the amount of alkali neutralized, the weight of phosphorus can be calculated. According to the equation for the reaction, 28 equivalents of alkali are required per atom of phosphorus:

1 ml. N/50 sodium hydroxide = 0.02214 mg. phosphorus.

Accurate results are obtained with quantities of phosphorus 0.01–10 mg.

Procedure when Arsenic is Present (Kuhn, loc. cit.).—Phosphorus may be determined in material also containing arsenic by the addition to 5 ml. of the phosphorus-arsenic solution of 10 ml. concentrated hydrochloric acid, 0.2 g. potassium bromide and 0.3 g. hydrazine sulfate and then distilling. The phosphorus is then determined nephelometrically or otherwise after previous destruction of the excess hydrazine with 0.5–1.0 ml. concentrated nitric acid.

Colorimetric Determination of Phosphorus and Arsenic.—When the amount of ammonium phosphomolybdate is so small that it cannot be weighed or titrated with accuracy the following Denigès [63] colorimetric method is used. If ferric iron is present in concentration greater than 4 to 6 parts per million, it interferes with the determination. If phosphorus and arsenic are both

[62] Richard Kuhn, Z. Physicl. Chem., **129**, 64 (1923); R. H. A. Plimmer, Biochem. J., **27**, 1810–13 (1933).

[63] Denigès, Compt. rend., **171**, 802 (1920); Troug and Meyer, Ind. Eng. Chem., Anal. Ed., **1**, 136 (1929).

present the two are first determined together. In a second sample the arsenic is reduced with hydrogen sulfide or a little sodium sulfide in acid solution. After boiling to drive off the excess of hydrogen sulfide, free sulfur is removed by adding pure filter paper pulp, shaking vigorously and filtering. The color due to the phosphorus alone is then developed. By difference the amount of arsenic may be obtained.

Preparation of Reagents: 1. ***Ammonium Molybdate-Sulfuric Acid Solution.*** —Dissolve 25 grams of ammonium molybdate in 200 ml. of water heated to 60° C. and filter. Dilute 280 ml. of arsenic and phosphorus-free concentrated sulfuric acid to 800 ml. After both solutions have cooled, the ammonium molybdate solution is added slowly, with shaking, to the sulfuric acid solution. After the combined solution has cooled to room temperature it is diluted with water to exactly 1000 ml. This is a 10 N sulfuric acid solution containing 2.5 grams of ammonium molybdate per 100 ml.

2. ***Stannous Chloride Solution.***—25 grams of stannous chloride crystals are dissolved in 1000 ml. of hydrochloric acid (sp.gr. 1.05). Filter if necessary. The solution should be protected from the air by floating a layer of white mineral oil about 5 mm. thick over the surface.

3. ***Standard Phosphate Solution.***—Dissolve 0.2195 gram of potassium dihydrogen phosphate and dilute to 1000 ml. A stock solution is made by taking 50 ml. of this and diluting to 500 ml. This stock solution contains 5 p.p.m. and is used for making the standard solution for comparison. To make this standard solution 5 ml. of the stock solution are taken, diluted to 95 ml. with distilled water, 4 ml. of the ammonium molybdate-sulfuric acid solution are added and thoroughly mixed by shaking in an Erlenmeyer flask. Six drops of stannous chloride are added and shaken. It is diluted to exactly 100 ml., shaken, and the solution is then ready for use. It contains 0.25 p.p.m. of phosphorus. For very dilute solutions 2 ml. of the stock solution are used, but the same amount of reagents, giving a standard which contains 0.1 p.p.m. of phosphorus. After standing 10 to 12 minutes, the standard will start to fade, and a drop more of stannous chloride should then be added to bring the full color back, which will again be permanent for 10 to 12 minutes.

Procedure.—In the analysis of water, water extracts of soils, minerals, fertilizers, etc., it is permissable to add the reagents directly to these unless they are colored, turbid, or decidedly acid or alkaline. Turbidity and color should be removed by appropriate means. A decidedly acid or alkaline reaction should be neutralized before adding the reagents. Organic materials may be ignited with magnesium nitrate. In this case it is best to keep the 10 N sulfuric acid and 2.5% ammonium molybdate as separate solutions, in order that the ignited residue may be dissolved with the sulfuric acid and the ammonium molybdate added after proper dilution. In all cases the reagents should be present after final dilution, in the proportion of 4 ml. of 10 N sulfuric acid, 4 ml. of 2.5% ammonium molybdate, and 6 drops of stannous chloride per 100 ml. The reagents should be thoroughly mixed with the test solution before the stannous chloride is added, after which thorough mixing should again be accomplished. Comparison with the standard should be made within 10 minutes after adding the stannous chloride. Blank tests should be run.

NOTES.—In work where maximum accuracy is required, the presence of much ferric iron will interfere with the results by decreasing the color intensity and giving troublesome greenish tints. By reducing the ferric iron in a Jones reductor, using metallic cadmium, these troubles are eliminated. The reduction should be made just previous to the addition of the ammonium molybdate.

Aluminum and manganous salts may be present in considerable quantity without influencing the color. Nitrate, as potassium nitrate, equivalent to 100 p.p.m. of nitrogen does not affect the color, while 200 p.p.m. reduces the intensity about 10%. Calcium oxide or magnesium oxide may be present up to 1000 p.p.m. without influence on the color.

THE MICROANALYTICAL DETERMINATION OF ARSENIC [64]

The substance is oxidized with sulfuric acid and "Perhydrol" and the arsenic precipitated with magnesia mixture.

Procedure.—5–10 mgm. of organic substance are placed in a micro-Kjeldahl flask with 4–5 drops of dilute sulfuric acid, heated, then cooled, 5 ml. of "Perhydrol" added, and again heated until fumes of sulfur trioxide are evolved. The oxidation is continued in the same way until after evaporation a clear solution is obtained. The solution is transferred to a glass dish of 30 to 40 ml. capacity and placed on a water bath, evaporated to dryness, then the residue is dissolved in 3 to 4 ml. of ammonia and treated while hot with 1 ml. of magnesia mixture (this is prepared by dissolving 5.5 gm. magnesium chloride crystals and 10.5 gm. ammonium chloride in 100 ml. of water). The magnesium ammonium arsenate which is precipitated is allowed to stand for 6 or preferably 12 hours at room temperature until it becomes crystalline.

The precipitate is then filtered through an ignited and weighed micro Neubauer or porcelain crucible, and alternately washed with a 3% solution of ammonia and alcohol with the aid of gentle suction. The crucible is removed and ignited. The residue of magnesium pyroarsenate still occludes magnesium salts, and must therefore again be washed repeatedly with a very dilute solution of ammonium hydroxide. After igniting strongly, the crucible is placed on a copper block and may be weighed after 10 minutes. The percentage of arsenic in the sample is calculated.

$$\text{Factor} \frac{2\text{As}}{\text{Mg}_2\text{As}_2\text{O}_7} = 0.4826.$$

A Volumetric Method for the Determination of Arsenic in Organic Substances.—The method [65] depends upon the fact that during the destruction of the organic substance arsenic is oxidized to arsenate; iodine is liberated from potassium iodide which can be titrated with sodium thiosulfate. The method

[64] "Abderhalden Handbuch d. Biochemischen Arbeitsmethoden," p. 727 (1919).

[65] Wintersteiner and Hannel, Mikrochemie, **4**, 155 (1926); also, Beamish and Collins, Ind. Eng. Chem., Anal. Ed., **6**, 379 (1934).

gives reliable results when halogens are absent in the organic substance and is particularly serviceable in elementary organic analysis. With halogens absent the average deviation from theory is ±0.2%, when titrating 2 to 4 mg. of arsenic.

Procedure.—7–12 mg. of substance are boiled with 1 ml. of 30% sulfuric acid and a few drops of concentrated nitric acid, more nitric acid is added and boiling continued. It is evaporated several times with the addition of a few drops of "Perhydrol," the residue is dissolved in 1 ml. of water, evaporated until sulfur trioxide is evolved, this process is repeated, then 1 ml. of water is added.

Beamish and Collins use a nickel microbomb for oxidizing the material. It is charged with a sample containing 1.5–3.0 mg. arsenic, 20–25 mg. (approx.) sucrose, and 1 gram (approx.) of sodium peroxide. The lid is clamped on, the contents thoroughly shaken, and tapped on the table to insure that all material is in the bottom of the bomb. Ignite by heating in the tip of a small hot flame for 35–40 seconds. Allow the bomb to stand in air for 5 seconds and then cool and rinse by immersing in cold distilled water. Remove the lid, wash it off into a pyrex tube, 35 mm. diameter and 155 mm. length, then add the cup and enough water to cover the cup. Heat to bring about solution of fusion and remove the cup with a nickel wire, and rinse thoroughly. The volume of solution should be 20–25 ml. and is evaporated to 10 ml., which also removes the hydrogen peroxide.

The procedure is now the same for both methods. To the cold solution 12 ml. of 12 N freshly boiled hydrochloric acid are added. To the solution at room temperature is added 1 ml. of freshly prepared 10% potassium iodide solution. Allow to stand for exactly 3 minutes and titrate the liberated iodine with 0.01 sodium thiosulfate. Near the end-point add starch indicator and titrate to the end-point. The color should not return for at least 5 minutes. A blank should be run for the reagent used and subtracted.

0.01 ml. of 0.01 N thiosulfate equals 0.00375 mg. of arsenic.

Arsenic in Cadavers.—The above method of O. Wintersteiner and H. Hannel has been modified for arsenic in cadavers.[66] The whole analysis should not take more than one and one-half hours and gives satisfactory results, with amounts of arsenic as low as 0.1 mg.

Procedure.—2 g. of material are employed and treated as described in the original method. The iron invariably present is determined in a portion of the solution colorimetrically. A correction for the amount of iron is subtracted from the titration value. Copper, if present, must be removed by the micro electrolytic method before determining the arsenic.

NOTE.—The results reported by Wintersteiner and Hannel are 0.02 mg. high when using samples containing 0.15–0.75 mg. arsenic trioxide, so that a sample should be taken which has an amount of arsenic not below 0.1 mg. and preferably twice this amount. This method should be of value because of the time saved in carrying out a determination.

Gutzeit Method.—Where small amounts of arsenic (0.001 to 0.04 mg.) are estimated, the Gutzeit method is recommended. There are a great number of modifications but for routine work, especially for arsenic in organic material,

[66] Szendro and Fleischer, Mikrochemie, Pregl Festschr., 321 (1929).

the method developed by C. E. Lachele [67] is recommended as being simple and giving reproducible results. It is applicable in the presence of impurities such as iron, tin, antimony, or reducible sulfur and in the presence of phosphorus compounds. Not over 30 mg. of antimony can be present. With modification, it is possible to analyze many products for arsenic using an undigested sample.

Reagents: ***Hydrochloric Acid.***—Make up 50 ml. of 35% arsenic-free hydrochloric acid to 100 ml. with water.

Stannous Chloride Solution.—Dissolve 40 grams of arsenic-free $SnCl_2 \cdot H_2O$ in concentrated hydrochloric acid and make up to 100 ml. with the same strength acid.

Mercuric Bromide Paper.—Carefully select filter sheets, similar to S and S No. 589 black ribbon paper, for weight and texture, and soak one hour in a saturated alcoholic solution of mercuric bromide. After sensitizing, remove sheets and dry by means of an air blast, and cut in disks of the same diameter as the diaphragm tube. Avoid touching the sensitized disks with the hands as far as possible. Disks should not be used when more than 5 or 6 days old.

Zinc.—Cut arsenic-free zinc in pieces about 1 cm. in length (approximately 5 grams). Activate the pieces by covering with hydrochloric acid (1 : 3) containing about 2 ml. of special stannous chloride solution for each 100 ml. of acid. Allow the action to continue for 15 minutes and wash well with distilled water.

Potassium Iodide Solution.—Dissolve 15 grams of potassium iodide in water and dilute to 100 ml.

Ferrous Ammonium Sulfate.—Use this substance or ferrous sulfate crystals free from arsenic.

Cuprous Chloride Solution.—Dissolve 15 grams of cuprous chloride in 100 ml. of 1 to 1 hydrochloric acid.

Cadmium Iodide Solution.—Dissolve 15 grams of cuprous chloride in 100 ml. of 1 to 1 hydrochloric acid.

Standard Arsenic Solution.—Dissolve 1 gram of arsenic trioxide in 25 ml. of 20% sodium hydroxide. Saturate the solution with carbon dioxide and dilute to 1 liter with recently boiled water. One ml. of this solution contains 1 mg. of arsenic trioxide. Dilute 40 ml. of this solution to 1 liter, diluting 50 ml. of the resulting solution to 1 liter. One ml. of this latter solution contains 0.002 mg. of arsenic trioxide and is used to prepare standard stains. Prepare fresh dilute solutions at frequent intervals.

Apparatus and Procedure.—Use an Erlenmeyer flask connected by a two-hole stopper to a Liebig or Allihn condenser. A gas such as nitrogen or hydrogen is introduced through a tube extending below the surface of the contents of the flask. The upper end of the condenser is packed with absorbent cotton, the lower half of which is saturated with the cuprous chloride solution which acts as a scrubber to remove impurities, such as phosphine, stibine, and hydrogen sulfide, from the evolved arsine. A chamber having a diameter that will accommodate a sensitized diaphragm of a size sufficient to combine with all the arsine is fitted to the condenser. The chamber consists of two thick-walled tubes of the same diameter, with ground-glass joints held together by an outside

[67] Ind. Eng. Chem., Anal. Ed., **6**, 256 (1934).

sleeve of Gooch rubber tubing. The impregnated paper is fitted between the two ground joints as pictured in Fig. 429.

An aliquot obtained from a sample digested with sulfuric and nitric acid in the usual manner (or the entire digestion in case of small amounts) is placed in a 1000 ml. Erlenmeyer flask with enough distilled water to make about 200 ml. of solution. Then 2 to 3 grams of solid ferrous ammonium sulfate or ferrous sulfate, 10 to 15 drops of stannous chloride solution and 50 ml. of 1 to 1 hydrochloric acid are added. Just before connecting to the condenser, introduce two or three pieces of activated zinc. A continual stream of nitrogen is kept flowing through the system to carry all traces of evolved arsine through the scrubber cotton to the paper diaphragm impregnated with mercuric bromide. The contents of the flask are boiled until all the arsine is evolved, which usually requires about 15 minutes. When the reaction is complete, the disk is removed and developed in cadmium iodide solution. This fixes the stain more permanently to light and water than does potassium iodide and changes the color from yellow to brown. The disk is allowed to remain in the iodide solution until all traces of red mercuric iodide, which immediately forms, have been dissolved. After prolonged use, the cadmium iodide solution turns yellow from the accumulation of complex cadmium mercuric iodides and should be replaced by fresh reagent. The excess reagent is removed from the disk by a water wash followed by a rinse with alcohol, and the disk is then dried between blotters. When dry, the stains are compared with standards. The standards are prepared in a similar manner to the unknowns in steps of 0.0025 mg. of arsenic trioxide, keeping them free from excess light exposure. The stains have a tendency to bleach slightly with age, and it is desirable to prepare fresh standards frequently, especially in the approximate range of the unknown.

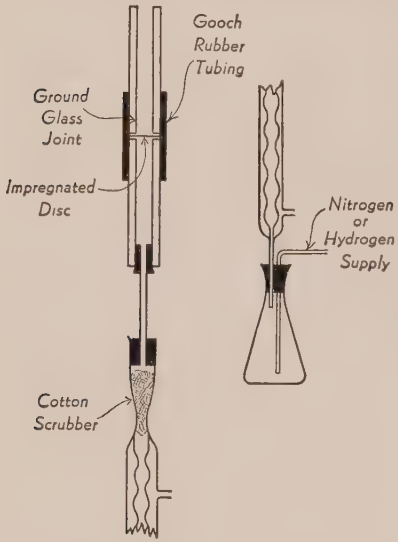

FIG. 429.

With some modifications, the method is applicable to the undigested material, thus shortening the total time of an arsenic determination to 15 to 30 minutes and eliminating the costly procedure of digestion with nitric and sulfuric acids.

From 5 to 100 grams of the undigested sample may be placed directly in the 1000 ml. Erlenmeyer flask together with 100 ml. of 1 to 1 hydrochloric acid, 1 to 2 ml. of stannous chloride solution, 15 ml. of potassium iodide solution, and 1 to 2 grams of solid ferrous sulfate. The activated zinc (3 or 4 pieces) is added, and the flask immediately connected to the condenser unit. The reaction is usually complete after 15 minutes of boiling, except that, when using large amounts of sample, a somewhat longer time may be necessary to evolve

all the arsine. The scrubber cotton should be saturated with a 15% solution of cuprous chloride in 1 to 1 hydrochloric acid to remove hydrogen sulfide, phosphine, and stibine, if present. [68] In case these gases have not been efficiently removed, the yellow stain imparted to the disk is not changed to brown when immersed in the cadmium iodide solution. When using large samples of some products that contain considerable reducible sulfur or phosphorus compounds, the scrubber cotton may not remove all impurities, and a preliminary treatment is necessary. The sample is heated a short time with an alkaline solution, after which it is slightly acidified with hydrochloric acid and the excess sulfide removed by boiling. The remaining sulfur and reduced phosphorus compounds are oxidized with bromine water, and then the bromine is removed by boiling before adding the sample to the reaction flask.

THE MICRODETERMINATION OF ORGANIC SULFUR

The material is burned in oxygen, the oxides of sulfur absorbed in "Perhydrol," and the sulfur precipitated as barium sulfate.

Apparatus.—The same apparatus is used as was described for the halogen determination.

Procedure.—The procedure is the same except that the spiral tube is filled with "Perhydrol," which has been diluted five times its volume with water. A 5–6 mg. sample is weighed and placed in the combustion tube, and the material slowly burned while the oxygen flows at the rate of 2 to 3 bubbles in 2 seconds. After combustion, the spiral filling is rinsed with 30 ml. of water into a pyrex beaker of 50 ml. capacity. One ml. freshly prepared 10% barium chloride solution added and 5 to 10 drops dilute hydrochloric acid. The dish is covered with a watch glass, evaporated to 5–10 ml. on a water bath, cooled, and the barium sulfate allowed to precipitate and settle for at least one hour, preferably overnight. The precipitate is transferred to a previously ignited and weighed micro porcelain filter crucible (or filter stick method may be used), gentle suction applied and alternately washed with alcohol and water. Water is used for the final washing. The precipitate is ignited, cooled, again washed, and one drop of dilute sulfuric acid added, and washed three times with pure water. It is again ignited, cooled on a copper block, and weighed to 0.005 mg.

Determination of Sulfur by Fusion.—A modification of the macro method employing potassium nitrate as the oxidizing agent is used.[69]

A fusion mixture which can be kept indefinitely is prepared by mixing four parts by weight of sodium carbonate with three parts of potassium nitrate and grinding to a fine powder.

[68] Where more than 30 mg. of antimony are present, a Milligan absorption bulb containing 100 ml. of special cuprous chloride solution should supplement the cotton scrubber.

[69] Harold Emerson, J. Am. Chem. Soc., **52**, 1291–2 (1930).

Procedure.—A finely powdered sample containing approximately 0.5 mg. of sulfur is weighed and mixed with 100 times its weight of the fusion mixture in a 20 ml. nickel crucible. A thin layer of the mixture is sprinkled on the top to prevent escape of sulfur fumes. A cover is placed on the crucible and it is set in a porcelain crucible of convenient size. Low heat with a Bunsen burner is applied for 10 minutes and full heat for 15 minutes. The contents of the crucible are cooled and dissolved in 5 ml. of warm water, filtered, the crucible and filter washed with 10 ml. of water and the sulfur precipitated with a 10% barium chloride solution as previously described on p. 2507.

NOTES.—(1) Elek and Hill [70] use a micro Parr bomb and use an explosion mixture as given on page 2496 note 2 for the determination of halogens. The fusion mixture is dissolved in 15 ml. of hot water. When cold 5 ml. concentrated hydrochloric acid are added to the solution. It is then filtered and the sulfur precipitated as barium sulfate in the usual manner.

(2) For routine work evaporation to 10–20 ml. is sufficient, and double ignition and treatment with sulfuric acid is not required.

(3) Funk and Kon [71] suggest using a 1% solution of barium chloride for precipitating the sulfur as barium sulfate in order to cut down occlusion, noted by Pregl in his method. This eliminates igniting the precipitate twice. They also describe a modification by which the determination of sulfur and halogen can be effected on a single sample of the substance.

The procedure in this case is somewhat modified. The halogen is absorbed in alkaline formaldehyde solution instead of sodium bisulfite. After the combustion is completed, the tube is washed out as usual, the solution acidified with acetic acid and the formaldehyde oxidized with "Perhydrol" by heating the mixture on a water bath. After the reaction is completed, the sulfuric acid formed is precipitated with a 1% barium acetate solution. The precipitation is completed by heating and the barium sulfate transferred to, ignited in, and weighed in a Neubauer or porcelain filter crucible; the test tube is washed out three or four times and the filtrate then removed and the silver chloride precipitated with silver nitrate as before.

(4) By adding picric acid [72] the particle size is increased and filtering can take place immediately, so that no time is lost in digestion and standing in order to complete precipitation. About 0.4 ml. of a saturated solution of picric acid is added per 15 ml. of solution. The solution is heated to near boiling, the picric acid added, then the barium chloride. After waiting a few minutes for the solution to cool, it is filtered and the precipitate ignited.

(5) Where the highest accuracy is not required, the barium sulfate, when picric acid is not used, can be dried at 150° C. and weighed. Some occlusion of mother liquor, of course, is present, and the results will tend to be high. With 2 mg. barium sulfate it is about 0.01 to 0.02 mg. high, when no other interfering elements are present except the original barium chloride. Those who wish to eliminate ignition must determine their error under the conditions with which they are working. It often happens that the accuracy is sufficient for the problem in question and the ignition is eliminated. The use of picric acid causes considerable occlusion so that ignition of the precipitate is required.

(6) Crucibles must be dried in an air oven at 120° C. before ignition, because spattering of the precipitate and cracking of the crucibles often results, if they are placed directly into the muffle.

Volumetric Determination of Sulfur.—In the absence of nitrogen or halogen in the original substance, the sulfuric acid instead of being precipitated as barium sulfate, is titrated with N/100 sodium hydroxide, using methyl red as an indicator.

[70] J. Am. Chem. Soc., **55**, 3479 (1933).
[71] J. Am. Chem. Soc., **48**, 1667 (1926).
[72] See Herbert Lindsly, Ind. Eng. Chem., Anal. Ed., **8**, 176–8 (1936).

If the "Perhydrol" used is not neutral it must be neutralized with sodium hydroxide using methyl red as the indicator.

The ter Meulen Hydrogenation Method (Volumetric).—The method [73] consists in burning the sample in hydrogen and absorbing the hydrogen sulfide which is formed in a solution of sodium hydroxide. An acidified standardized solution of iodine is added and the iodine remaining after the reaction with the liberated hydrogen sulfide is titrated with thiosulfate. The method has not been used by a sufficient number of investigators to evaluate it as a standard procedure. It is, therefore, described here in order to bring it to the attention of those who may wish to try out the method. From the published results and the author's experience with a limited number of compounds, it seems to offer a simple rapid volumetric method where a high degree of accuracy is not required. Other microvolumetric procedures for sulfur which have been published have not proven satisfactory. Where a high degree of accuracy is required, the gravimetric procedure of weighing the sulfur as barium sulfate must be employed.

Results by the ter Meulen method usually vary $\pm 0.2\%$ from theory when using samples of organic material containing 1–3 mg. of sulfur.

Solutions.

0.02 N Iodine.
0.02 N Thiosulfate.
0.2 N Hydrochloric Acid (approximately).
Starch Indicator Solution.
0.05 N Sodium Hydroxide Solution (approximately).

Apparatus.—A glass or preferably silica combustion tube, such as is used for carbon and hydrogen, is filled for a distance of 10 cm. with 5% platinized asbestos. A simple gas absorption bulb for the hydrogen sulfide, Fig. 430, and a purifying train for the hydrogen, complete the setup. The hydrogen may be generated from hydrochloric acid and zinc or be taken from a cylinder.

Fig. 430.

Procedure.—A boat with a sample containing 1–3 mg. of sulfur is placed in the combustion tube. The platinum catalyst is heated to 700–750° C. The air in the combustion tube is swept out with hydrogen. The hydrogen passes through the tube during the actual combustion at the rate of 500 ml. in 30 minutes. The sample is slowly burned by moving the furnace or burner over the sample. The total time of burning should take 20 minutes. The tube

[73] H. ter Meulen, Rec. trav. chim., **41**, 112 (1922); Chem. weekblad, **23**, 348 (1926), 19 (1930) and Goswami and Sarkar, J. Ind. Chem. Soc., **10**, 611 (1933).

is then swept out for another 25 minutes while the boat is kept at red heat (700–750° C.). The hydrogen sulfide is absorbed in 4 ml. of sodium hydroxide and, at the completion of the run, this is washed with boiled water into a 125 ml. Erlenmeyer flask containing 6–7 ml. of iodine and 4 ml. of hydrochloric acid, and diluted with 10 ml. of water. The total volume of the solution should not be over 30 to 40 ml. The excess iodine is titrated with 0.02 N thiosulfate and the percentage of sulfur is calculated.

1 ml. of 0.02 N iodine = 0.3206 mg. sulfur.

The iodine solution is standardized against the thiosulfate.

Notes.—(1) The sulfur in most organic compounds is quantitatively reduced to hydrogen sulfide with platinized asbestos, but occasionally some, according to ter Meulen, require a catalyst of platinum foil or a 6 inch roll of 80 mesh platinum gauze for rapid conversion. If platinized asbestos is used with such compounds, the sample must be burned very slowly and with extreme care.[74] If metallic platinum is used, the presence of nitrogen in the sample causes the formation of hydrogen cyanide which acts the same as hydrogen sulfide thus giving high results. In order, therefore, to prevent the absorption of hydrogen cyanide, a solution of dilute zinc sulfate, approximately 0.05 N, to which is added sodium acetate, approximately 0.05 N, and a drop of acetic acid must be used. As before, iodine together with dilute hydrochloric acid, is added, and when all the zinc sulfide has disappeared, the excess iodine is titrated with thiosulfate.

(2) ter Meulen also states that platinum black (prepared by reducing at a low temperature ammonium chloroplatinate with hydrogen) must be mixed with petroleum in order to get complete conversion of sulfur to hydrogen sulfide. This catalyst must be freshly prepared, as heating in air causes a diminishing of its activity.

(3) When a zinc sulfate solution is used and zinc sulfide is precipitated, the spiral type of absorber shown in Fig. 430 cannot be used because of the difficulty in washing out the precipitate. In such a case it is best to omit the spiral and make the bore of the stopcock at the bottom sufficiently large, so that the precipitate can be easily rinsed out. The Pregl type of absorption tube used with the methoxyl ethoxy apparatus, Fig. 438, is also satisfactory.

(4) After 5–6 runs, oxygen must be passed through the tube in order to burn out the organic matter and regenerate the catalyst. To prevent the danger of an explosion, carbon dioxide should be passed through first to sweep out the hydrogen.

MICROELECTROANALYSIS

The Microelectrolytic Cell of Clarke and Hermance.[75]—A cell for micro electroanalysis has recently been constructed which permits more effective agitation of the solution during electrolysis than can be accomplished by the Pregl method of boiling, or allowing the solution to cool during the period of electrolysis. The cell is constructed so that the solution is agitated by a jet of air and the solution maintained at a suitable temperature by a water jacket heated with a micro burner. While the cell is more difficult to construct than

[74] Rec. Trav. Chim., **53**, 121 (1934).
[75] J. Am. Chem. Soc., **54**, 877 (1932).

that of Pregl, it yields accurate results even when the deposit on the electrode weighs 1 mg. The average results reported are 0.1% higher than theory. The individual determinations had an average deviation of ±0.2–0.3% from the amount recovered.

Apparatus.—The large outer vessel (Fig. 431) sealed to the electrode compartment at its base is a water-jacket which can be heated by a micro-flame. Figure 432–I shows the glass frame which in the assembled cell fits inside the electrode vessel and serves to support both the electrodes and pumping device.

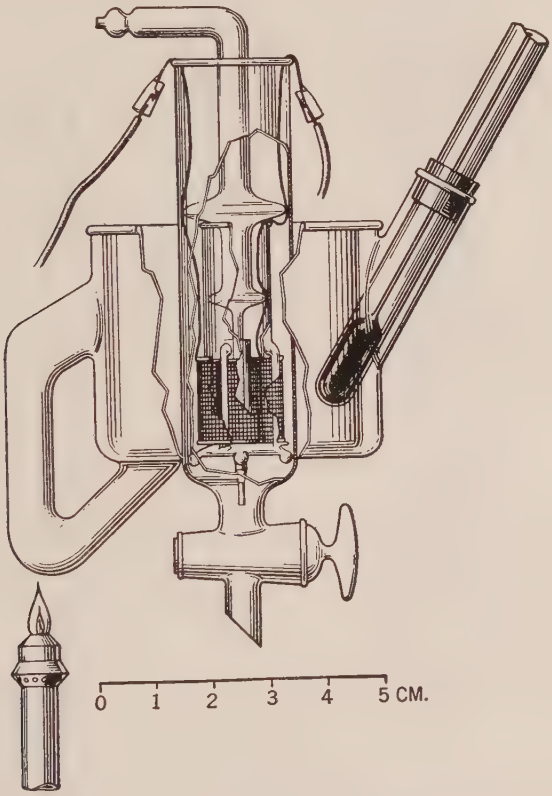

Fig. 431.

Its lower end is flared to form a conical bell having a diameter about 4 mm. less than that of the container. While the two electrodes are held very close together, they cannot make contact or become fouled by touching the glass wall of the container. The support permits a free circulation of the electrolyte. This circulation is accomplished by the tube shown in Fig. 432–II, which is held erect in the axis of the cell. A stream of bubbles of air or inert gas is introduced by means of this tube into the space under the bell and causes a continuous overflow of liquid over the top of the tube *A* that supports the inner

electrode. At the same time, the suction caused by the removal of the liquid from under the bell further assists circulation in this direction by drawing upon that portion of the electrolyte in the space between the outer electrode and the wall of the containing vessel. A rapid agitation is thus maintained whereby the whole of the electrolyte is forced through the inter-electrode space several times a minute.

"The electrodes are two platinum gauze cylinders 15 mm. high, the one having an inside diameter of 9 mm., the other 18 mm., weighing 0.8 g., and 1.5 g., respectively."

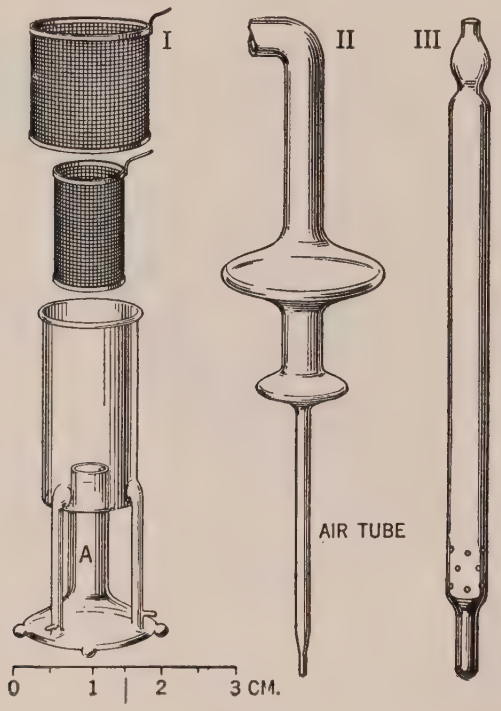

Fig. 432.

Procedure.—The electrodes are cleaned with hot concentrated nitric acid, rinsed with distilled water, dried by heating to dull redness over the Bunsen flame, then cooled and weighed. The electrodes are assembled (Fig. 432-I) and the unit lowered into the cell vessel containing the solution to be electrolyzed, the volume of which (about 5 ml.) is then so adjusted that its level coincides with the upper end of the tube *A* in Fig. 432-I. The air tube is now introduced as indicated, and air admitted at such a rate that the liquid may be seen to flow regularly over the top of the tube *A*. The electrical connections are made and the electrolysis begins. The deposition is completed when the current falls to a negligible value. The re-solution of the deposit is overcome

by washing and withdrawing the electrodes without interrupting the current. The electrolyte is drained from the cell by opening the stopcock at the bottom and at the same time distilled water is admitted at the top of the cell.

If the electrolyzed solution is to be used for the determination of other constituents, excessive dilution with wash water is objectionable and the device shown in Fig. 432-III is used, which minimizes the quantity of wash water when only the inner electrode is to be weighed.

At the completion of the electrolysis, the air tube is withdrawn and this perforated tube is inserted in the tube *A* (Fig. 432-I) and connected to a reservoir containing distilled water. The cell is slowly drained as before, and wash water admitted through the tube at the same rate. At the same time and without interrupting the current, the electrode is drawn up over the tube *A* until it occupies a position level with the perforations on the washing tube. The electrode held in this position is withdrawn together with the washing tube from the electrolyte. At the time it is pulled through the liquid surface it is surrounded by nearly pure wash water. If the holes in the washing tube are sufficiently fine and the operations executed rapidly and skillfully the electrolyte suffers a minimum amount of dilution. After removal from the cell the deposit is further washed with water, alcohol and ether, and then dried in an oven at a temperature of 90° C. unless different directions are given. The electrode is protected from dust while cooling, and is finally weighed.

Determination of Metals Using the Cell of Clarke and Hermance: ***Determination of Nickel.***—To a 5 ml. solution containing 1 mg. of nickel 0.2 g. ammonium sulfate and 1.7 ml. concentrated ammonia solution are added. The air used for stirring is passed through a concentrated ammonia solution, which serves to prevent loss of ammonia from the electrolyte. The conditions for deposition are: e.m.f. 2.4–2.5 volts (60–70 Milliamperes); temperature 60° C.; time 15 to 20 minutes.

Determination of Zinc.—The deposition is made from a potassium hydroxide solution. The deposit assumes a granular form if the temperature is too high, the alkali content too low, or if hydrogen is evolved at the cathode. The conditions which must be rigidly maintained are: potassium hydroxide concentration 10%; e.m.f. 3 volts (150 Milliamperes); temperature 25° C.; time 15 minutes.

Notes.—The cathodic evolution of hydrogen is prevented by giving the platinum gauze a thin preliminary coat of copper. Since the zinc deposit is very soluble in 10% caustic solution, special care must be taken to wash out all traces of electrolyte before interrupting the current.

Determination of Tin.—As recommended by A. Fischer [76] the electrode is first prepared by depositing a thin coat of copper, followed by one of tin from an oxalate solution. The electrolyte consists of ammonium monosulfide solution containing sodium sulfite. The best conditions for electrolysis are: e.m.f. 1.2 volts (1200 Milliamperes); temperature 60° C.; time 20 to 30 minutes. After electrolysis the electrode is washed with water, alcohol, carbon bisulfide, alcohol, and ether, in the order given.

Notes.—The copper plate should contain about two tenths of a milligram of the metal, plated from dilute nitric acid solution containing sulfuric acid. The electrolyte

[76] Z. anorg. Chem., **42**, 367 (1904).

should contain 2% sulfuric acid and 1% nitric acid. Temperature 70–75° C.; e.m.f. 3.5 volts; time to deposit 1 mg. about 20 minutes.

The thin plate of tin is next deposited. The electrolyte consists of 5 ml. of a solution made up to contain 3.6 gm. of ammonium oxalate, 3.6 gms. of oxalic acid and 100 mg. of tin as stannous chloride, in 100 ml. of water. The solution is electrolyzed at an e.m.f. of 3.0–3.8 volts; temperature 25° C. The electrolysis is continued until a bright coating of tin is obtained over the copper. The electrode is then removed, washed with water, acetone, dried at 70–80° C. and weighed.

In the determination of the unknown the tin is dissolved in hydrochloric acid, the solution evaporated to remove the excess acid, and the moist residue redissolved in 1 ml. of water. Four ml. of the ammonium monosulfide solution are then added, and the electrolysis carried out. The monosulfide solution is prepared as follows: Concentrated aqueous ammonia is saturated with hydrogen sulfide gas, followed by the addition of an equal volume of ammonia. Sixteen ml. of the resulting solution are diluted to 120 ml., and 8 gms. of sodium sulfite added. The solution should always be freshly prepared.

The Determination of Traces of Metal Impurities by the Method of Clarke and Hermance.—It often happens that the volume of a solution is large, relative to the metal concentration and cannot be reduced owing to high salt concentration. The apparatus described below may be used to effect a separation of the trace of metal present in the large volume, and the deposit, if

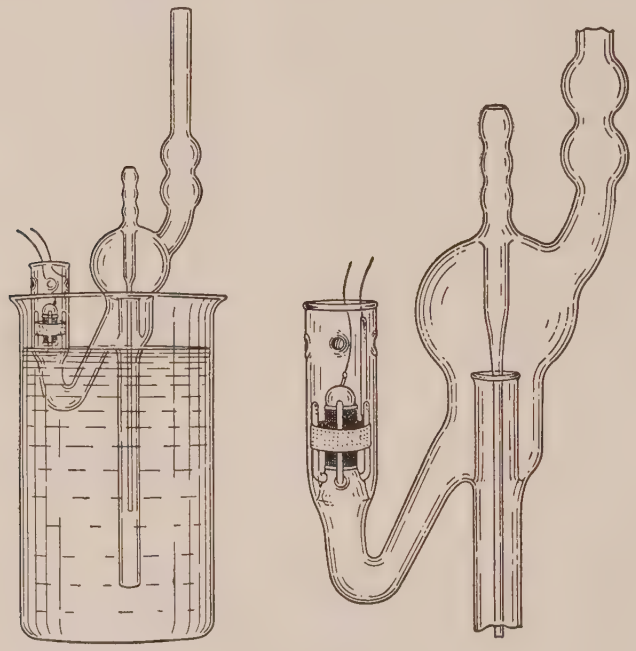

Fig. 433.

contaminated with other material, is redissolved and the final quantitative determination carried out in the small micro cell previously described.

The apparatus,[77] consists of a combination of air lift and micro electrolysis

[77] Clarke and Hermance, Mikrochemie, 20, 126–8 (1936).

chamber constructed in a single assembly. This may be used in beakers, tanks, or vessels of almost any description regardless of size, provided there is a sufficient depth of liquid to accommodate the pump tube. The liquid continuously raised to a height several cm. above the level of that in the container, flows from a small reservoir into the cell containing the electrode assembly. In this chamber a platinum gauze electrode cylinder rests directly above the inlet tube and is held in position by four glass prongs, spaced at equal intervals around it. A solid glass ball is placed in the upper open end of this electrode to divert the inflowing liquid through its meshes. The outer electrode, also cylindrical, is held concentrically about the inner one by the 4 prongs over which it is slipped into position. The liquid flows out through small holes in the cell wall near the top. By having the electrolysis chamber independent of the air pump and the containing chamber, the electrode assembly is readily accessible for adjustment, observation, or removal of either electrode. Washing is effectively carried out by simply stopping the pump and flushing out the chamber with a stream of water introduced below the electrode level, from a suitable nozzle. With this apparatus, 0.1 mg. of copper was quantitatively recovered from a volume of 20,000 ml. This solution was 0.1 molar sodium sulfate and 0.1 M sulfuric acid.

Determination of Traces of Zinc in Aluminum Solutions.—To 250 ml. of solution is added enough potassium hydroxide to redissolve the aluminum and furnish 5% in excess. The solution is electrolyzed for four hours at room temperature, at 3.5 volts. If iron is present, it will deposit with the zinc. The impure deposit is redissolved and the iron precipitated as the hydroxide between pH 4 and 5. The zinc is then replated from the filtrate on a coppered electrode using the small cell.

Determination of Lead in the Presence of Zinc.—To 250 ml. of solution 2% of nitric acid, and 25 mg. of copper sulfate are added. The latter functions as a depolarizer which increases the hydrogen overvoltage and prevents cathodic reduction of the quadrivalent lead. The conditions for electrolysis are: e.m.f. 2.8 volts; temperature 60–70° C.; time 3 hours. The final determination of the plated lead is made volumetrically as recommended by Lucas and Grassner.[78] The deposited lead is brought into solution with 1 ml. of 10% potassium iodide solution and a drop of concentrated acetic acid. Several crystals of sodium acetate are then added and the solution rinsed into a small flask with a stopper. The iodine that is liberated is titrated with 0.001 N sodium thiosulfate solution (titrate back with N/1000 iodine solution). A micro burette of 2 ml. capacity graduated in 0.01 ml. is used. 0.100 ml. N/1000 sodium thiosulfate solution corresponds to 10.36 gamma lead (0.01036 mg.).

NOTES.—(1) Weighing amounts of lead as low as 0.5 mg. directly as lead dioxide may be accomplished with the following procedure:[79] The electrodes are formed of 1 inch sq. platinum foil, 0.09 mm. in thickness, to which platinum wire is welded. They are corrugated and etched with aqua regia. The lead is deposited under the following conditions: Two drops of sulfuric acid, 4.5 ml. of 15–20% nitric acid in 30 ml. of solution, temperature of 85–90° C., electrolysis at 5.5 amperes per square decimeter for 2 hours.

The above authors found that even when using large electrodes (8.75 sq. in.) by first coating with about 0.05 gm. of lead dioxide, they could successfully determine small

[78] Mikrochemie, "Emich Festschr.," p. 199 (1930).

[79] Day, Delano, and Schrenk, School of Mines and Metallurgy, Univ. of Missouri Bull., **12**, No. 2, pages 37–41 (1935).

amounts of lead. Conditions are as follows: 25 ml. of free nitric acid, 0.25 ml. of sulfuric acid in 140 ml. of solution. This was heated up to 85–90° C. and electrolyzed at 5.5 amperes per square decimeter for 2 hours. The difference in weight before and after electrolysis is the weight of the new deposit. 0.0010 mg. of lead dioxide was determined with a maximum deviation of 0.0001 mg. Another method which was successfully used, was adding known amounts of lead dioxide to the unknown sample; for example, 10 mg., which amount can then be accurately determined. The amount of lead dioxide over that added, gives the amount present in the sample.

A. J. Lindsey [80] deposits from a solution containing not over 6 mg. of lead using 2 ml. concentrated nitric acid and total volume of solution of 12 ml. The solution is heated nearly to boiling and stirred with a gas stream of nitrogen. It is electrolyzed at 1.0 volt (current 120–200 milliamperes) for 7 minutes. The sides of the cell are washed down and electrolysis is continued for 3 minutes.

Determination of Traces of Copper in Nickel Solutions.—To 250 ml. of solution containing 1% nitric acid and 2% sulfuric acid, a potential of 3 volts is applied for 4 hours with the solution at a temperature of 60°–70° C. The copper plate is dissolved and redeposited in the small cell and weighed.

Notes.—Okac [81] has also improved the Pregl cell along the same lines as have Clarke and Hermance. Carbon dioxide is passed into the solution through an anode tube during electrolysis and after deposition is completed, the cathode is washed by admitting water through the same tube.

The electrolyte for all depositions is an ammonium hydroxide solution with a volume of 5–6 ml. containing 0.5–1.5 ml. of concentrated ammonia. The electrolysis takes place at room temperature. The results reported have an average deviation from theory of ±0.01 mg. when the amount of metal deposited is 0.5 to 5 mg., which is not equal to the accuracy when using the other procedures described. The method is illustrated by the following two determinations:

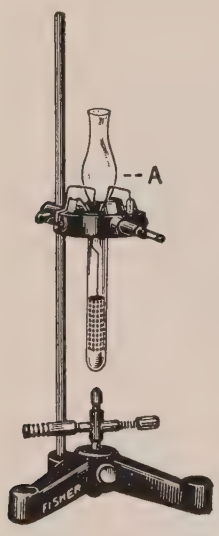

Fig. 434.

Cadmium.—Six ml. of a cadmium sulfate solution containing 1 to 3 mg. of cadmium and 1.5 ml. concentrated ammonia are electrolyzed. Conditions for electrolysis are: volts 3; Milliamperes 20–30 (0.1–0.15 Amp./q.d.m.); time 10 minutes; temperature 20° C.

Mercury.—Six ml. of a solution containing 0.5 to 15 mg. of mercury as the nitrate or chloride, and 1 ml. of concentrated ammonia are electrolyzed. A platinum gauze cathode is used. Conditions for electrolysis are: volts 2.4–2.5; Milliamperes 20–100 (0.1–0.5 Amp./q.d.m.); time 10 minutes; temperature 20° C. The cathode is washed with water, alcohol, and ether, and dried over calcium chloride for one hour.

The Pregl Cell.—This cell is readily constructed from materials in the laboratory and for those who only occasionally need an electrolytic cell, it is adequate. Typical determinations using this cell are given, but of course the methods may be used also with the Clarke and Hermance apparatus and vice versa.

A general view of the apparatus is shown in Fig. 434. The platinum gauze cathode, Fig. 435, is 10 mm. in diameter and 30 mm. in length, with a stout platinum wire 100 mm. in length welded to it. Three small glass beads are sealed to

[80] Analyst, **60**, 744–6 (1935).
[81] Z. Anal. Chem., **88**, 108, 189, 431 (1932); **89**, 106 (1932).

the upper and three to the lower edge of the gauze to prevent contact with the sides of the cell during withdrawal.

The anode is a platinum wire 130 mm. in length (Fig. 435), to which two glass extensions are sealed so that it may be more easily kept in the center of the cell.

The cell consists of a test tube, 16 mm. in diameter, and 105 mm. in length. The terminals of the electrodes are bent so as to make contact by dipping into mercury (Fig. 434).

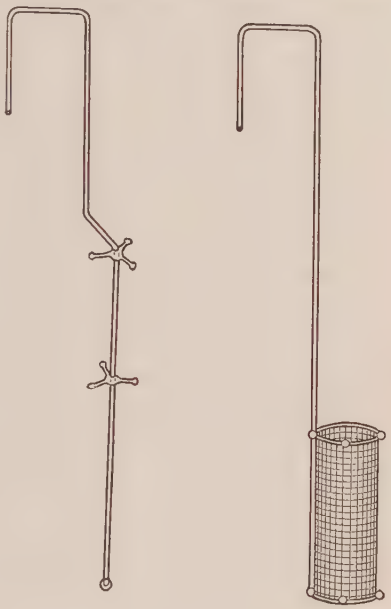

Fig. 435.

Procedure.—The gauze cathode is successively dipped into hot concentrated nitric acid, water, alcohol, and ether, then dried over the Bunsen flame or in an electric oven, cooled, and weighed.

Determination of Metals Using the Pregl Cell: ***Determination of Copper in Alloys.***[82]—The material is brought into solution with concentrated nitric acid. The amount of copper present for each determination should be about 10 mg. and the volume of the solution 5 to 6 ml. If the alloy is high in copper, an aliquot of the original solution is taken for electrolysis.

The cell is assembled, the solution added, and heated to boiling. The current is turned on, and electrolysis takes place with an e.m.f. of 2.7 to 3.1 volts. The flame is removed and the solution allowed to cool during electrolysis. If the concentration of nitric acid is too high, deposition will not take place, and in this case a crystal or so of potassium sulfate is added; and if this is not sufficient, ammonia solution is added drop by drop until deposition begins. A drop of alcohol added to the solution at the commencement of the determination will prevent spraying due to evolution of gas at the anode. A few minutes after electrolysis begins, the walls of the cell should be rinsed free of any traces of electrolyte with a few drops of 1% nitric acid solution.

After 25 minutes the deposition should be complete, and without interrupting the current, remove first the anode, then the cathode, and wash the copper deposit with distilled water. If lead has been present it will be deposited on the anode and may be removed with nitric and oxalic acid. Benedetti-Pichler recommends that only water should be used to wash the deposited copper if it appears spongy, as alcohol tends to cause a flaking off. It is then dried at 90° C., cooled and weighed.

Notes.—(1) In order to keep the volume of the solution constant during electrolysis, water must be added or a water condenser (A in Fig. 434) used.

(2) Where electrolysis is carried out in sulfuric acid solution, the time is shortened by 10 to 15 minutes and in many determinations there is nothing to prevent the use of

[82] Benedetti-Pichler, Z. Anal. Chem., **62**, 321 (1923).

sulfuric acid. One drop of concentrated acid in 5 ml. of solution is sufficient and an e.m.f. of 2 volts is maintained. Where organic matter is present in the electrolyte, the metal is deposited in the regular manner, but in order to free the deposit from impurities, the electrodes are removed, fresh electrolyte placed in the cell, the electrodes again assembled, and the current reversed so that the metal goes back into solution. The current is again changed and the metal redeposited.

The Determination of Mercury.[83]—The method will determine 0.1 to 0.9 mg. of mercury with an average deviation from theory of ± 0.003 mg.

Dissolve the metal in 0.5 to 2 ml. of concentrated nitric acid, transfer to a measuring flask, and take an aliquot of the diluted solution for electrolysis. The cell is a small narrow vessel larger than the Pregl cell and holds 8 to 20 ml. The cathode is a gold wire 8 cm. in length and 0.3 mm. in diameter and the anode a platinum wire formed in a spiral. Conditions for electrolysis are: acidity 0.1 N; current 0.015–0.08 amperes; e.m.f. 3 volts; time 15–20 hours; temperature 20° C. The electrodes are removed without interrupting the current, and the cathode carefully washed with water, dried over phosphorus pentoxide for 3 hours, and then weighed. To remove the mercury, the cathode is heated carefully over a small flame.

Notes.—Verdino [84] uses the Pregl cell and a gold plated platinum gauze cathode prepared as follows: 50 mg. of gold are dissolved in aqua regia and the solution evaporated to dryness several times with water to remove the excess acid. The residue is finally dissolved in 5 ml. of water containing 0.65 g. of pure potassium cyanide. The gold is deposited at an e.m.f. of 3.5 volts; temperature 55° C.; time 2 hours.

The organic material containing 2 to 5 mg. of mercury is placed in a small hard glass tube, and 10 drops of fuming nitric acid added. The tube is sealed and placed in a bomb for 2 hours at 270–280° C. After cooling, the tube is broken and the contents rinsed into the electrolytic cell with 5 ml. of water. The conditions for electrolysis are: e.m.f. 3.5 volts; temperature 40° C.; time 40 minutes. Acidity in the ratio of 1 ml. concentrated nitric acid to 9 ml. of water—or 5 ml. of electrolyte should contain 0.5 ml. concentrated nitric acid. Before removing the electrodes the cell is cooled for 5 minutes with cold water. The cathode is washed with water, alcohol, and ether. It is dried by waving in the air and weighed. If the deposit is contaminated with organic matter, it should be redeposited in fresh electrolyte.

The Determination of Gold.[85]—It is possible to obtain excellent results with a solution containing less than 0.5 g. gold per liter, using a volume as small as 0.5 ml. and electrolyzing from a potassium cyanide solution which is the same procedure as given for gold plating the platinum cathode in the determination of mercury outlined above.

Fuchs suggests covering the solution with a little toluene to protect the anode from possible attack by chlorine. The temperature of the solution should be close to boiling and a current of 3 amperes at 3–3.5 volts is suitable.

The Determination of Silver.[86]—The total volume of aqueous solution is 7 ml. to which are added a few drops of concentrated sulfuric acid, and 1 ml. of 20% tartaric acid. If a wet oxidation to recover the silver has been carried out, the acid concentration should be reduced by evaporation to less than 1 ml. Conditions for electrolysis are: 1.3–1.4 volts for 15 minutes, then 1.8 volts for 30 minutes. A sample containing 1–4 mg. of silver is best, but samples containing as low as 32 γ are reported as being accurately analyzed.

[83] F. Patat, Mikrochemie, New Series, **5**, 16 (1932).
[84] Mikrochemie, **6**, 5 (1928).
[85] Fuchs, Mikrochemie, **1**, 86 (1923).
[86] Friederick and Rapoport, Mikrochemie, **18**, 227–34 (1935).

Copper in Organic and Biological Material.—In many cases the amount of copper is too small to be determined by weighing, so that a colorimetric method is required The following methods have been critically studied and are accurate within the limits indicated.

Ashing.—A sample containing 0.02 to 0.05 mg. of copper is ashed in a porcelain, or preferably platinum or silica dish in an electric furnace at a temperature of 510–565° C. for 3 to 4 hours or until a clean whitish-grey ash is obtained. In the case of a liquid it must be evaporated before ashing. The addition of 5 drops of glacial acetic acid added to 250 ml. of milk speeds up the process of evaporation and prevents frothing.

Treatment of Ash.—(1) Copper may be separated from the ash by micro electrolytic deposition. From 0.02 to 0.05 mg. of copper should be present. The ash is dissolved in 1 : 1 nitric acid and added to the electrolytic cell as described under microelectrolytic analysis. The voltage should be kept between 2.7 to 2.1. If the copper deposit is contaminated with other metals, it is best to reverse the current in fresh 1% nitric acid and redeposit. If the amount of copper is 0.5 mg. or more, it may be weighed directly. If not, it can be dissolved in acid and treated by any of the colorimetric methods described below.

(2) The ash may be treated directly by the Biazzo method if impurities, such as iron, which interfere with the colorimetric procedure are absent. If such impurities are present, then the copper must be precipitated as the sulfide.

(3) Without copper sulfide precipitation.

The ash is taken up in 15 ml. of 1 : 1 hydrochloric acid. The solution is evaporated in order to render the silica insoluble, the residue moistened with 5 ml. of hydrochloric acid and 5 ml. of water added. It is then warmed on a sand bath for ½ hour, filtered, the residue washed thoroughly with water to a volume of 100 ml., evaporated to 10 ml., cooled and transferred to a 25 ml. volumetric flask.

(4) With copper sulfide precipitation.

Ferric iron when present in large amounts gives a brownish tinge to the chloroform layer. The iron is removed by taking up the ash with 10 ml. of 1 : 1 hydrochloric acid, diluted and filtered. The iron is reduced by adding granulated zinc, copper free, and the solution boiled until it is colorless. It is then filtered, the filtrate made up to a volume of 200 ml. which gives a solution of about 1% acid concentration. Hydrogen sulfide is passed into the warm solution for 15 minutes and the precipitation vessel kept stoppered until the copper sulfide settles. The precipitate may be allowed to settle out overnight. The copper sulfide is now filtered off or it may be centrifuged. The filter and precipitate are disintegrated in 5 ml. of nitric acid. The solution is diluted, brought to boiling, the paper filtered off, and evaporated at 10 ml., and is then treated by one of the procedures outlined below.

The Biazzo Method.[87]—The method is based upon the fact that a neutral solution of a copper salt when treated with a few drops of pyridine and potassium thiocyanide gives a green precipitate of the composition $Cu(C_5H_5N)_2(CNS)_2$ which is soluble in chloroform. It gives accurate results with amounts of 50 to 150 γ.

[87] R. Biazzo, Ann. Chim. Appl., **16**, 2 (1926); C. A. Elvehjem and W. C. Lindow, J. Biol. Chem., **81**, 435 (1929).

Preparation of Standards.—A copper sulfate solution is prepared containing 0.1 mg. of copper in 1 ml. of solution by dissolving 0.3928 gm. pure $CuSO_45H_2O$ in water and diluting to a liter. The crystals must not show signs of efflorescence. Then 0.5, 1, and 2 ml. of this standard solution are treated with acetic acid, potassium thiocyanate, pyridine, and chloroform in exactly the same manner as the sample solution and made up to 25 ml. A standard is chosen which has approximately the same intensity as the sample.

One N sodium hydroxide is added to make solution just alkaline to phenolphthalein, 1 ml. glacial acetic acid added, 1 ml. 10% potassium thiocyanate solution, 10 drops pyridine, 5 ml. chloroform, *accurately measured*, and made up to volume. The solution is shaken, the chloroform layer allowed to settle to the bottom of the flask, and most of the aqueous layer is removed. The remaining chloroform and water layer is transferred to a Bausch and Lomb colorimeter and the color is compared to a standard similarly prepared.

NOTES.—(1) In a critical study of the micromethods proposed for the determination of copper in organic material, Ansbacher, Remington, and Culp [88] found that better results were obtained if the chloroform in the colorimetric determination was replaced by bromobenzene as proposed by Kleinmann and Klinke.[89]

An aliquot of the neutral solution is placed in separatory funnel, add 10 ml. of water, 25 drops of glacial acetic acid, 30 drops of pyridine, 3 ml. (10%) of potassium thiocyanate, and 2 ml. of bromobenzene (b.p. 154–155° C.), and the original procedure is followed. These workers report that the most satisfactory results were obtained when the amount of copper in the bromobenzene layer was 50 to 150 γ (0.050 to 0.150 mg.).

Carbamate Colorimetric Method.—This method [90] gives accurate results with 1 γ to 5 γ copper with an accuracy of 0.2 γ.

After obtaining the electrolytic copper or copper sulfide as described before, it is dissolved in a few drops of concentrated nitric acid and heated on a water bath for a few minutes. The sample is cooled, diluted to 5 ml., and 1 ml. of 20% ammonium hydroxide added or enough to give a distinct odor. The solution is cooled, made up to exactly 10 ml. and thoroughly mixed. It is then centrifuged for 10 minutes to remove any turbidity which may have appeared with the addition of ammonia and poured into another tube. An aliquot containing 0.001 to 0.005 mg. of copper is taken for the colorimetric determination. Two ml. of ammonia are added and the volume is brought to 10 ml., 1 ml. of 0.1% aqueous solution of sodium diethyldithiocarbamate is added and the solution mixed well. The yellow color is compared immediately with the color in a set of standards prepared in the same manner from a copper sultion containing 1 mg. of copper per ml. The standard should be freshly prepared for each set of determinations from an accurately standardized stock solution containing 1 mg. of copper per ml. Quantities of copper below 0.001 mg. cannot be accurately determined.

NOTES.—(1) Ignition vessels, especially new porcelain, should be treated by adding an alcoholic solution of sodium acetate equivalent to 1 gm. of the salt, followed by ignition in an electric furnace with subsequent extraction in 1 : 1 hydrochloric acid for a period of several days. All reagents, including filter paper, should be carefully checked to see that they are not a source of contamination.

[88] Ind. Eng. Chem., Anal. Ed., **3**, 314 (1931).
[89] Arch. path. Anat., **275**, 422 (1930).
[90] Conn and co-workers, Ind. Eng. Chem., Anal. Ed., **7**, 15 (1935).

(2) Both the electrolytic and sulfide method are effective in separating the copper from its impurities. Conn and co-workers recovered 97% by the precipitation method and 98% by the microelectrolytic method, but the copper sulfide method will recover smaller amounts of copper—as low as 0.002 gm.

(3) If undestroyed carbon remains after the period of ashing, it is filtered off, returned to the quartz dish and again ashed.

GRAVIMETRIC DETERMINATION OF NICKEL AND COPPER

Brunck's dimethyl glyoxime method is followed.[91] The nickel content of the sample should be from 0.1–4.0 mg. in order to obtain accurate results. The original sample containing nickel is brought into solution by any of the well-known procedures. Benedetti-Pichler using 1–1.5 mg. of nickel ammonium sulfate, obtained an average deviation of −0.05 from the theoretical nickel percentage of 14.86.

Procedure.—2–3 ml. of the solution to be analyzed are transferred to a precipitating flask which has been thoroughly cleansed with chromic acid. A few drops of ammonium hydroxide, so that the solution turns blue, and a slight excess of 1% dimethylglyoxime in alcohol are added; usually 4 to 5 drops are sufficient. The precipitate is digested for about 30 minutes at 70° and then filtered off with the aid of the filter tube or filter crucible used for halogen determination. The precipitate is washed 2–3 times with a little hot water. If copper is to be determined this filtrate is saved. The washing is continued, using hot 3% ammonia solution in order to remove all the soluble salts from the precipitate, finally washed with alcohol, and dried to constant weight at 105° C. If iron is present it should be reduced with sulfur dioxide.

Copper.—Copper, if present, may be determined from the first filtrate by adding 3–4 drops of 1% benzoin oxime solution in alcohol. The precipitate is digested on the water bath for 30 minutes, filtered and the precipitate washed with 3% ammonia and finally with 50% alcohol, then dried to constant weight at 105° C. The precipitate $(C_{14}H_{11}O_2N)Cu$ contains 22.02% copper. The solution should contain little if any ammonium salt.

Another excellent method for the determination of copper is by the use of 5,7–dibrom-8-hydroxyquinoline $(C_9H_4Br_2ON)_2Cu$.[92] The test solution is evaporated to dryness in a weighed micro beaker with filter stick, and taken up in 0.1–0.2 ml. of dilute (1 : 10) nitric acid, and a few tenths of a ml. of hot water until the volume is around 2 ml. Then 0.1 ml. of acetone is added and the beaker warmed to 50° C. A saturated acetone solution of dibromo-8-hydroxyquinoline (about 0.3%) is added drop by drop. Every 0.1 mg. of copper oxide requires about 1 ml. of reagent to give the usual 3 to 4 times excess. After 10

[91] O. Brunck, Z. angew. Chem., **20**, 834; Strebinger and Pollak, Mikrochemie, **2**, 125 (1924); Benedetti-Pichler, Mettalu u. Erz., **25**, 206 (1928).

[92] F. Hecht and R. Reissner, Mikrochem, **17**, 127–34 (1935); R. Berg, "Mikrochem. Emich festschrift," 26 (1930).

minutes on a gently boiling water bath the mixture is filtered warm, and the precipitate is washed three times with wash liquid (0.4 ml. of 6.5% nitric acid and 15 ml. of acetone diluted to 20 ml. with water), and dried for an hour at 110–115° C. The method is suitable for amounts up to 1 mg. of copper $(C_9H_4Br_2ON)_2Cu$ contains 9.53% copper.

VOLUMETRIC DETERMINATION OF IRON [93]

The material containing iron is brought into solution, preferably with hydrochloric acid, reduced, and titrated in the presence of carbon dioxide with potassium dichromate using diphenylamine as the indicator. Because the oxidation of diphenylamine is catalyzed by the presence of ferric ions, a small amount of ferric chloride must always be added if traces of ferrous iron are to be titrated. The average deviation from theory when titrating 0.2–0.5 mg. of iron is ±0.002 mg.

Reagents.—Solution 1—5 g. ferric chloride plus 6 ml. concentrated sulfuric acid with water to make 100 ml.

Solution 2—7 ml. phosphoric acid (sp.gr. 1.76) with water to make 100 ml.

A stannous chloride solution containing 8 mg. stannous chloride per ml.

A saturated mercuric chloride solution.

An N/250 potassium dichromate solution.

Indicator—0.1 g. diphenylamine in 100 ml. of concentrated sulfuric acid.

Procedure.—A sample of material containing 0.2–0.5 mg. of iron is weighed and brought into solution with hydrochloric acid. The vessel used for solution and titration is a test tube 16 mm. in diameter and 10 cm. high. The solution is heated to boiling and stannous chloride is added drop by drop until the solution is colorless and then one drop in excess. The sides of the vessel are rinsed with 4–6 drops of water—the total volume of the solution should be 1–2 ml. Carbon dioxide free from air is now passed through the solution for 5 minutes using a capillary tube. Without interrupting the gas stream, 0.2 ml. of a cold saturated solution of mercuric chloride is added. The precipitate formed should have a white silky appearance. If a black precipitate results, too much stannous chloride has been added and metallic mercury is present, and the determination is spoiled. With the gas stream bubbling slowly through the solution 1.5 ml. solution 1 are added, then 1 ml. solution 2, and 3 drops of indicator, and the titration commenced using N/250 potassium dichromate and a micro burette. The appearance of the final color blue violet marks the end-point. In a blank experiment without the ferrous salt, the amount of dichromate solution necessary for the color change is determined. This amount is deducted as a correction and the percentage of iron in the sample

[93] J. Knop, J. Am. Chem. Soc., **46**, 263 (1924); Benedetti-Pichler, Z. Anal. Chem., **73**, 200 (1928).

calculated. One ml. of N/250 potassium dichromate solution equals 0.223 mg. of iron.

NOTES.—Knop and Kubelkova [94] in a study of indicators suitable for titrating small amounts of iron with potassium permanganate have found that by using suitable indicators 1 mg. of iron can be titrated with an accuracy of 0.1 to 0.5%. Among the suitable indicators are Erioglaucin A and Eriogrun B. No indicator correction is required. When chloride is present in the solution it is necessary to have about 0.2 g. of manganous salt present to prevent destruction of the dyestuff because of induced oxidation. An excess of indicator up to four times the amount necessary to impart a distinct color only causes an error of 0.3% when 1 mg. of iron is titrated with 0.005 N potassium permanganate solution.

DETERMINATION OF ACETYL

The methods for the determination of acetyl generally involve a preliminary hydrolysis, followed by a determination of the liberated acetic acid. All the methods proposed have their limitations when applied to the analysis of all types of compounds. The following two methods, however, are given together with the types of compounds for which they are best suited.

The Method of Elek and Harte.[95]—The hydrolysis is performed with aqueous p-toluene sulfonic acid, followed by distillation in vacuo. The sulfur dioxide and acetic acid are measured by iodometric titrations. The method is applicable to o-acetyl and n-acetyl compounds, except where more than one volatile acid is produced by hydrolysis, in which case the results are excessively high.

Apparatus.—"The apparatus, as shown in Fig. 436, is constructed wholly of Pyrex glass, with the joints especially ground to be vacuum tight with only water as lubricant. The connection between the side arm of the flask and the condenser is glass to glass, sheathed in steamed rubber tubing in order to provide sufficient flexibility to permit tapping the flask. It is important, therefore, that these parts be made of the same diameter tubing.

"The whole apparatus, with the exception of the rubber connection which is well steamed, is thoroughly cleaned with chromic acid cleaning mixture, well rinsed, and dried before using. Between successive determinations thorough rinsing with distilled water is sufficient and only the flask need be dried."

Solutions:

1. 25% aqueous solution of p-toluene sulfonic acid.
2. 0.01 N sodium thiosulfate.
3. 0.01 N iodine.
4. 4% potassium iodate.
5. Starch indicator.

Procedure.—"A well-ground and thoroughly dried sample of from 4 to 10 mg., accurately weighed by difference on a microbalance, is placed on the

[94] Z. Anal. Chem., **85**, 401 (1931).
[95] Ind. Eng. Chem., Anal. Ed., **8**, 267 (1936).

bottom of the hydrolyzing flask, preferably using a long-handled charging tube. The flask is then filled about three-quarters full with short pieces (4 to 5 mm. each) of 4 mm. Pyrex rod. The funnel, wet on the ground joint with distilled water, is inserted and fastened with short wire springs. Two milliliters of the

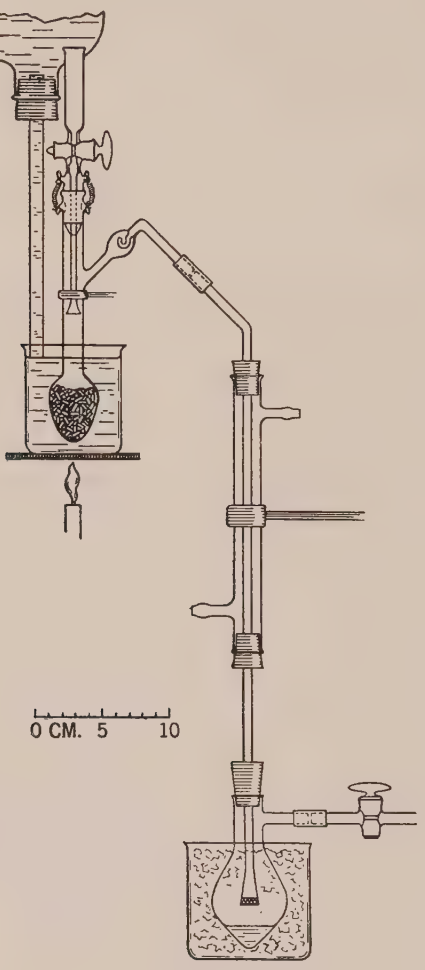

Fig. 436.

sulfonic acid reagent are then added through the funnel and the closed stopcock is sealed with 2 to 3 drops of distilled water added through the funnel. In the analysis of halogen-containing compounds, a few milligrams of silver sulfate should be added.

"The side arm of the flask is connected to the condenser by means of the

freshly rinsed short section of rubber tubing, a glass-to-glass joint being easily effected. The receiving flask, previously charged with 5 ml. of the 0.01 N iodine solution with 1 to 1.5 grams of potassium iodide (conveniently measured out as a powder by means of a small marked test tube) dissolved therein, is attached to the rubber stopper on the lower end of the condenser and adjusted so that the sintered plate is about 1 cm. above the surface of the liquid. The side arm of the receiver is capped with a well-washed rubber nipple. The receiver, up to the side arm, is cooled by immersion in a beaker of finely cracked ice, renewed from time to time during the hydrolysis after removal of the water formed by the melting. A stream of cold water is circulated through the jacket of the condenser. The flask is tapped sufficiently to mix the sample intimately with the acid.

"An asbestos board is placed as a shield between the burner and the condenser. The mixture is heated by bringing the water in the surrounding beaker to boiling. The level of water in the beaker is maintained during the period of heating by using an inverted bottle containing water, held well above the apparatus, and having a 1 cm. tube reaching just to the desired level in the beaker.

"During the course of the heating, the flask is vigorously tapped at intervals in order to agitate its contents. Hydrolysis is continued for 1 hour for o-acetyl and 2.5 to 3 hours for n-acetyl compounds. Where the nature of the linkage is unknown the longer period is, of course, to be employed. At the end of the hydrolysis, the hot water is siphoned out of the beaker and replaced by ice cold water. After leaving the apparatus to cool for about 5 minutes, an aspirator is connected through a manometer and stopcock to the side arm of the receiver and the system is evacuated to a pressure of 50 to 60 mm. The receiver is lifted, together with its cooling beaker, until the sintered plate is about 2 mm. from the bottom of the receiver and the water surrounding the hydrolyzing flask is heated. At first a few very small bubbles are seen to pass through the iodine solution, but the bubbling stops in a few seconds as the pressure is equalized throughout the system. When the fluid in the flask has completely distilled over, aided by occasional tapping, about 1.5 ml. of water are run in through the funnel without either breaking the vacuum or stopping the heating. After the contents of the flask have become dry, a second, and finally a third portion of water is introduced in a similar manner. Heating is then continued until the contents of the flask are completely dry and for 5 to 10 minutes thereafter. The receiver is then lowered, using a gentle rotatory motion, until the sintered plate is 2 to 3 cm. above the fluid. The stopcock between the receiver and the gage is closed; the connection between the stopcock and the gage is broken, and then by slowly opening the stopcock the system is brought back to atmospheric pressure, and the burner is extinguished.

"The condenser is disconnected from the flask and washed through three times with small volumes of distilled water, flow across the sintered plate being aided by the application of suction through the side arm of the receiver. The outside of the lower part of the condenser is washed into the receiver with distilled water; the total volume should be about half its capacity. The solution in the receiver whose side arm is capped with the rubber nipple, is titrated with the standard thiosulfate, using 2 drops of the starch indicator added toward the end of the titration. To the now colorless solution about 2 ml. of the

potassium iodate solution are added, and the receiver is immediately stoppered with a soda-lime tube, placed in a beaker of water at about 35° C., and allowed to stand for 20 minutes. At the end of that time the solution is titrated with the thiosulfate solution, the end-point being taken where the blue color which develops during the titration just disappears.

"The value from the initial titration is to be subtracted from the value obtained by titration of 5 ml. of the iodine solution in which 1 to 1.5 grams of the potassium iodide are dissolved and 2 to 3 drops of dilute acetic acid added. (It is especially important when measuring the iodine solution from a microburet to wait 1 to 2 minutes before reading the buret; the drainage error may otherwise be considerable.) This latter titration should not be made until the mixture has stood for about 5 minutes at room temperature. The difference so calculated is a correction for the sulfur dioxide and varies from 0.00 to 0.05 ml. Where it exceeds the upper limit the analysis should be rejected. The difference, doubled to account for the dibasicity of the sulfuric acid formed, is deducted from the final titration as a correction for the acid introduced as sulfurdioxide."

Calculation: The acetyl content is given by the formula

$$\%CH_3CO = 10 \times \frac{\text{volume of thiosulfate (corr.)} \times \text{factor of solution} \times 0.4302}{\text{weight of sample}}$$

Method of Robinson and Bailey.—This simple method [96] is an adaptation of the well-known macro method. It is applicable to compounds which do not possess acidic functions either in themselves or as a result of alkali splitting.

Procedure.—A 5–10 mg. sample is weighed into a small porcelain boat and introduced into a 20 ml. Pyrex flask. Five ml. of N/25 aqueous sodium hydroxide are added to the flask, and a micro reflux condenser attached. The solution is boiled gently for 12 to 35 hours. The time required for complete hydrolysis depends largely upon the character of its acetyl linkage. It has been found that the acetyl N linkage possesses greater stability than the acetyl-O linkage. After hydrolysis is complete, any alkali adhering to the condenser and rubber stopper is washed into the flask and the excess alkali titrated with N/100 hydrochloric acid using phenolphthalein as the indicator. A blank correction as determined by a control experiment is necessary. The accuracy of the method is equal or better than that of Pregl-Soltys or Kuhn-Roth [97] methods. The results are usually low, 0.06 to 0.20, from the theoretical percentages.

[96] Mikrochemie, **15**, 233 (1934).
[97] Ber., **66**, 1274 (1933).

THE DETERMINATION OF METHOXYL-ETHOXYL

The micromethod uses a modified Zeisel procedure. The RI may be collected in alcoholic silver nitrate and weighed as silver iodide or it may be titrated according to Vieböck and Schwappach.[98] The titration method may be used in the presence of sulfur. The method is based upon the following reaction: $R^1OR+HI\rightarrow R^1OH+RI$. The volumetric procedure is based upon the following reactions:

$$CH_3I+Br_2\rightarrow CH_3Br+IBr.$$
$$IBr+2Br_2+3H_2O\rightarrow HIO_3+5HBr.$$

The accuracy of the method is $\pm 0.1\%$ from the theoretical percentage.

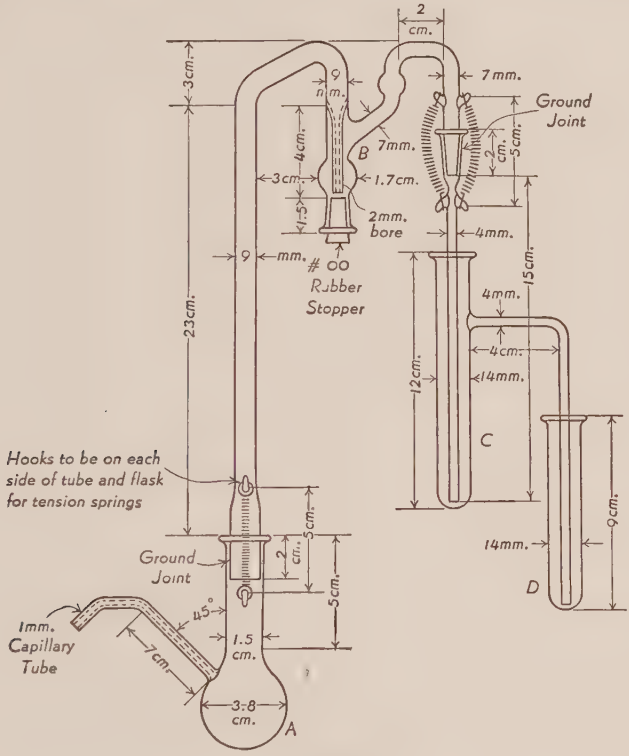

Fig. 437.

Apparatus.—The apparatus described [99] is typical of most and may be used for either micro or macro determinations. It is constructed of Pyrex glass and the details are given by Fig. 437.

[98] Ber., **63**, 2818 (1930); Viebock and Brecher, Ber., **63**, 3207 (1930).
[99] E. P. Clark, J. A. O. A. C., **15**, 136 (1932).

Reagents.—Formic acid, 90–100%.
Analytically pure sodium acetate.
Iodate free potassium iodide.
Red phosphorus.
0.02 N thiosulfate.
Constant boiling hydriodic acid, 57% (store in the dark).
Indicators—starch, methyl red.

Procedure.—Five to ten mg. of dried sample or an amount equal to 3–5 ml. of thiosulfate are weighed into a small glass capsule which will readily slip into the decomposition flask *A*. A boiling rod is placed in the flask. 2.5 ml. of melted analytical quality phenol and 5 ml. of constant boiling hydriodic acid are added. The flask is then connected with the remainder of the apparatus which consists of scrubber *B*, containing a little water and the receivers, *C* and *D*. The receivers contain 10 ml. of a 10% glacial acetic acid solution of potassium acetate to which 6 drops of bromine have been added. Approximately 6 ml. of the solution is placed in *C* and 4 ml. in *D*. (See Note (14).)

A slow uniform stream of carbon dioxide is passed through the capillary sidearm of the boiling flask and the liquid is gently heated by means of a mantled micro burner at such a rate that the vapors of the boiling liquid rise half-way up the condenser. For most substances, 30 minutes are sufficient to complete the reaction and sweep out the apparatus. The contents of both receivers are washed into a 250 ml. Erlenmeyer flask which contains 5 ml. of a 25% aqueous sodium acetate solution. The volume of the liquid is then adjusted to approximately 125 ml. and 6 drops of 90% formic acid added. The flask is rotated until the color due to the bromine is discharged, then 12 more drops of formic acid are added, and the solution is allowed to stand for 1 to 2 minutes. One gm. of potassium iodide and a few ml. of 10% sulfuric acid are next added and the free iodine titrated with 0.02 N thiosulfate. A blank should be run on the reagents, as phenol contains some substance which gives a small blank.

Calculation.—31.03 parts of methoxyl or 45.05 parts of ethoxyl yields 6 atoms or 761.5 parts of iodine.

One ml. 0.02 N thiosulfate = 0.1034 mg. methoxyl or 0.1501 mg. ethoxyl.

Notes.—(1) The boiling rod is a glass tube approximately 60 mm. long and 3.5 mm. outside diameter with 1 mm. bore. It is sealed at one end and also closed about 10 mm. from the other. The open end is fire polished. When this is placed in the flask with the open end down it will induce uniform boiling as long as sufficient heat is constantly applied to the liquid.

(2) The hydriodic acid employed usually contains more or less free iodine resulting from the decomposition of the hydriodic acid. A permanently colorless solution of hydriodic acid may be obtained if the liquid heated to approximately 100° C. is treated with slightly more than the necessary quantity of 50% hypophosphorous acid. When a hydriodic acid solution thus treated is used for alkoxyl determination, no free iodine will be evolved and consequently no phosphorus need be employed in the scrubber B.

(3) Gibson and Caulfield [100] have studied the Viebock procedure and advocate the following absorbing solution. It should be freshly prepared by adding 6 drops (0.05 ml.) of bromine to 18 ml. of 20% aqueous potassium bromide. One-half of this serves as a blank and is kept beside the absorption tubes during the estimation, being titrated under the same conditions at the end. The remaining absorption solution is filled into two

[100] J. Chem. Soc., **1935**, 1419–20.

absorption tubes, 7.5 ml. into the first, and 1.5 ml. into the second. The absorption tubes and the blank are immersed in ice water during the estimation.

(4) White and Wright [101] studied the modification of Gibson and Caulfield and find that the largest error is the action of light on the bromine in the absorbing bromine-potassium bromide solution. They use the same procedure as Gibson and Caulfield, but simplify the absorption train by using only one receiver. The fig. 438 shows the regular Pregl type absorption tube but modified as follows: Before the outlet tube from the apparatus is inserted into one of the receivers, a glass sleeve *H* is placed at *I*. When the assembly is complete, the sleeve *H* is allowed to fall so that it rests on the constriction of the receiver as shown. This sleeve, about 1.5 cm. long, is cut from glass tubing about 1 ml. larger than the tube forming the bottom of the receiver and is notched 4 times around the periphery of the edges with a wet file. When the sleeve is correctly made, it permits free circulation between the top and the bottom of the receiver and yet it will retain the ascending bubble of gas long enough to facilitate absorption. Tufts of cotton are placed in the mouths of the receiver.

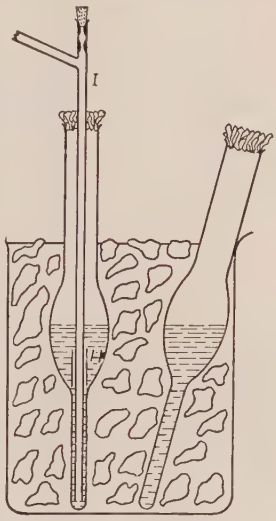

Fig. 438.

Another method is to use a glass spiral which fits snugly against the wall of the absorption tube and the tube *I*, so that the ascending bubbles follow the spiral. A stopcock may be sealed to the bottom of the absorption tube and the contents washed into the flask without removing the tube from the apparatus.

(5) If on the addition of formic acid the bromine does not disappear, it indicates that insufficient sodium acetate was used.

(6) If several determinations are to be run at once, the same charge of hydriodic acid and phenol may be used for all of them, but a fresh boiling rod should be used for each determination and the blank due to the phenol should be subtracted only from the first run as the material responsible for the blank is destroyed during the first run. This matter, however, should be checked to make certain that such is the case.

(7) If the hydriodic acid contains free iodine, this must be removed by putting a water suspension of finely divided red phosphorus in the scrubber *B*. The apparatus should be so constructed and operated that no red phosphorus goes over into the absorption tubes and thus ruins the determination.

(8) The time of heating varies with different compounds but there are few that take over one hour.

(9) The procedure should be standardized as to time and volume of solutions, so that a constant blank may be obtained for any particular apparatus.

(10) The carbon dioxide from cylinders may be pure enough for use without a purifying train. If halides are present, they should be removed by a solution of silver nitrate and the gas dried by passing through a dehydrating agent.

(11) An oil bath can be used to heat the flask A, but for rapid routine work the use of a micro burner is preferable.

(12) The determination of N linked to CH_3 methylimide can be determined after the ethoxyl methoxyl has distilled over at 135° C. The method is tedious and not satisfactory as a routine determination. The method as given by Slotta and Haberland [102] uses the same apparatus as for the alkyloxyl determination, except two bulbs as traps, Fig. 439, are inserted in the distilling tube. The flask is charged with 3–5 mg. sample, 2 granules red phosphorus, 1.5 ml. hydriodic acid, 30–100 mg. ammonium iodide, and a small amount of phenol. The gas washer is filled with a 1.5% sodium thiosulfate solution containing 0.5% sodium carbonate. The procedure is then carried out as described previously in order to distill off any alkoxyl. The scrubber and the receivers are re-

[101] Can. Journ. Res., **14**, 427 (1936).
[102] Ber., 65B, No. 1, 127–9 (1932).

charged and the flask heated to 350° C. The hydriodic acid distills over into the trap and the methylimide comes off and is carried over by the stream of carbon dioxide. After heating for one hour with carbon dioxide flowing, the flask is cooled to 200° C., the hydriodic acid is sucked back into the flask and the flask is again heated to 350° C. The solution in the receiver is titrated as for alkoxyl. A third heating should not yield a titratable amount in the receivers.

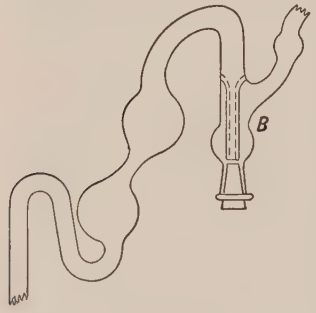

Fig. 439.

(13) Where a compound yields both methyl and ethyl iodide, a separation may be made:

A. By the combustion method of A. Friederich.[102a] The total percentage of methoxy and ethoxy is first determined. Then, from another sample, the distilled methyl and ethyl iodide is led into a microcombustion furnace and the percentage of carbon determined. The proportion of oxygen atoms to carbon atoms can then be calculated. If a methoxy group is present, the ratio of oxygen to carbon is 1 : 1; an ethoxy group, if 1 : 2; and if 2 : 3, the proportion of methoxy to ethoxy is 1 : 1.

B. By absorbing the alkyl iodides in an alcoholic solution of tetramethylamine.[102b] The receivers are charged with approximately 5 ml. each of a 10% solution (by weight) of anhydrous trimethylamine in absolute ethanol and 10 ml. of absolute ethanol. After the run, the absorption tubes are stoppered and allowed to stand for 24 hours. Separation is effected by taking advantage of the relative insolubility of tetramethylammonium iodide in absolute alcohol (the trimethylethylammonium iodide is 100 times more soluble). For accurate work a correction is made for the loss by solubility of tetramethylammonium iodide and the amount of loss is best determined by each operator under the experimental conditions used. The precipitate is dissolved in hot water, 3–5 drops conc. nitric acid are added and the methoxy is determined by adding silver nitrate and weighing the silver iodide. In the same way the ethoxy in the filtrate from the trimethylamine separation is determined.

(14) 0.3–0.5 ml. acetic anhydride may also be added to the reaction mixture in flask *A*.

THE DETERMINATION OF MOLECULAR WEIGHT

For Solids—By Rise of the Boiling Point.—The following is a micro modification of the method developed by Menzies and Wright.[103] There are two forms of the apparatus, the chief difference being that in one the solvent is boiled by a small coil of platinum wire placed directly in the solvent [104] while in the other a small gas or alcohol flame is used.[105] Fig. 440 shows the bottom of the boiling tube with platinum coil, and Fig. 441 shows the Smith and Milner apparatus. Both are the same except for the lower section. By using a

[102a] A. Friederich, *Mikrochemie*, **7**, 185 (1929).

[102b] Willstätter and Utzinger, *Ann. Chem.*, **382**, 148 (1911). Küster and Maag, *Z. Physiol. Chem.*, **127**, 190 (1923). Phillips and Goss, *J. A. O. A. C.*, **20**, 292 (1937).

[103] J. Am. Chem. Soc., **43**, 2314 (1921).

[104] A. F. Colson, Analyst, **57**, 757 (1932).

[105] Smith and Milner, Mikrochemie, **9**, 117 (1931).

differential thermometer the observed change in boiling point is much larger than when a microBeckmann is used, and changes in pressure do not affect the determination. The volume of solvent is determined, which is not done with other microforms of apparatus using the rise of the boiling point method. Therefore, more accurate results are possible.

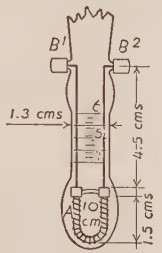

Fig. 440.

Apparatus.—Fig. 441–I. *T* is the boiling tube; *S*, vacuum jacket; *F*, the boiling bulb, 3.0 ml. capacity to large mark. The neck *G* is graduated in 0.1 ml.; *W*, tungsten wire; b_1 and b_2, enlargements to accommodate thermometer bulbs. Fig. 441–II Cu, copper spiral; *L*, etched millimeter scales; B_1 and B_2, thermometer bulbs Fig. 441–III *P*, Cottrel pump. The differential thermometer may be made in the laboratory or purchased.

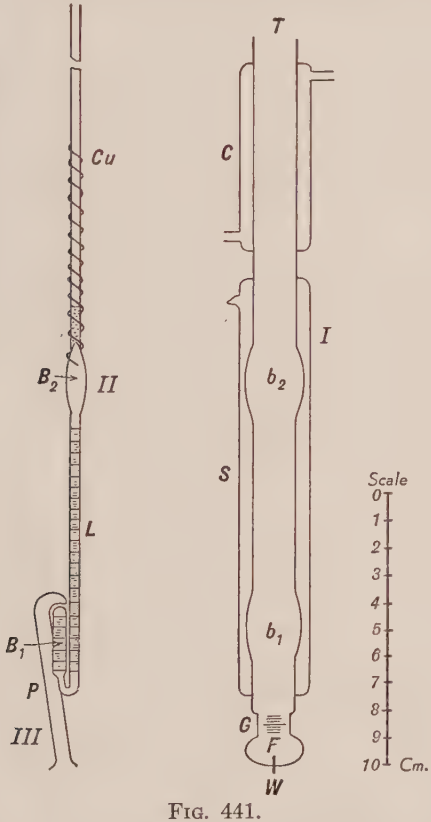

Fig. 441.

Procedure.—The boiling tube is clamped in a vertical position and an asbestos board 10 cm. square with a 5 mm. hole in its center, is placed under the boiling tube so that the tungsten wire, *W*, protrudes through the hole. This wire is sealed through the bottom of the boiling tube and enables the liquid to boil without bumping and directs the bubbles of vapor through the pump. Water is then started through the condenser and 3.00 ml. of solvent are pipetted into the bulb *F*. A micro burner or alcohol lamp is placed directly under the tungsten wire and so adjusted that the liquid will reflux gently from the condenser. A standard thermometer is then inserted into the vapors and the true boiling point of the solvent determined to the nearest 0.1°. The amount of solvent actually present in the bulb *F* is then determined by removing the burner, quickly checking the ebullition by touching the bottom of *F* with a beaker of water and immediately reading the volume of the solvent from the graduation *G*, which has been previously calibrated.

The standard thermometer is then removed and the apparatus assembled for the determination of the rise of the boiling point. The pump is lowered over the tungsten wire. The differential thermometer is then clamped in such a position that its lower bulb is directly under the opening of the pump, but not in contact with it. The thermometer should not touch any portion of the boiling tube. The burner

is then returned to its original position and the liquid boiled briskly enough to pump it in an almost continuous stream over the lower bulb of the thermometer. Then at intervals of 1 or 2 minutes, readings are made on the millimeter scales etched on the thermometer. When the readings have become constant, they are recorded. The sample, 10–15 mg., made into the form of a pellet in a pellet press, is accurately weighed and is then introduced into the boiling tube. Again the thermometer liquid is allowed to become constant and the reading recorded. This may require 5–10 minutes. Additional pellets may then be introduced and the corresponding records made.

Calculation.—For the conversion table of the differential thermometer the original paper should be consulted.[106] The ebullioscopic constant, K_1, is for one mole of solute in 100 gm. of solvent. This requires also knowing the density of the solvent at its boiling point. The ebullioscopic constant, K_2, is for one mole of solute in 100 ml. of solvent at its boiling point.

$$K_1 = \frac{\text{Rise B.P.} \times \text{molecular wt. of solute} \times \text{wt. of solvent}}{100 \times \text{wt. of solute}},$$

$$K_2 = \frac{\text{Rise B.P.} \times \text{molecular wt. of solute} \times \text{ml. of solvent}}{100 \times \text{wt. of solute}}.$$

Constants Useful in Ebullioscopy

J. Am. Chem. Soc., **43**, 2320 (1921)

Solvent	B.P. ° C.	dp/dt	D	dD/dt	K_1	K_2
Acetone	57.0	26.4	0.7522	0.0011	17.2	22.9
Benzene	80.1	23.4	0.8149	0.0010	26.1	32.0
Carbon disulfide	46.3	24.7	1.2223	0.0016	23.7	19.4
Carbon tetrachloride	76.8	23.3	1.4801	0.0021	48.0	32.4
Chloroform	61.2	25.2	1.4101	0.0018	39.0	27.7
Ethyl acetate	77.2	25.1	0.8302	0.0010	27.9	33.6
Ethyl alcohol	78.4	30.3	0.7389	0.0011	11.7	15.8
Ethyl ether	34.6	26.9	0.6968	0.0011	21.6	31.1
Methyl acetate	57.1	26.8	0.8802	0.0014	20.6	23.4
Methyl alcohol	64.7	29.6	0.7468	0.0010	8.8	11.8

NOTES.—The following precautions should be taken:

(1) An almost continuous stream of liquid must be pumped over the lower bulb of the differential thermometer, and most of the ebullition takes place through the pump.

(2) That the flame be shielded from draughts to prevent fluctuations of the thermometer readings.

(3) That the upper bulb of the differential thermometer be well laved by the condensed solvent flowing down the copper spiral. Colson (loc. cit.) has at the top two copper wires touching the wall of the boiling tube near the edge of the condenser, which directs the liquid onto the copper coil on the thermometer stem.

(4) Water should not be allowed to condense from the atmosphere onto the inner surface of the boiling tube. This is best accomplished by circulating water at room temperature through the condenser at a constant rate of about 4 ml. per minute.

With the above precautions the differential thermometer can be read with an accuracy of 0.1 mm. and the volume of the solvent in the bulb F to 0.03 ml.

[106] Menzies, J. Am. Chem. Soc., **43**, 2309 (1921).

(5) If the molecular weight of a non volatile viscous liquid is to be obtained, the liquid may be introduced into the apparatus in a small glass tube, 2×15 mm., constricted to a pin point opening at one end. When introduced into the boiling tube the solvent will quickly remove the solute from such a tube, yet the tube will retain the sample during the weighing.

(6) When the solvent is boiled, by the method of Colson (loc. cit.) the problem of superheating, bumping and shielding the burner from air currents is avoided. The reading of the volume is taken the moment the current is shut off. No momentary cooling with a beaker of water is necessary, thus giving greater accuracy in the volume reading.

(7) The apparatus of Sucharda and Bobranski [107] and of Rieche [107] use the micro Beckmann thermometer and an attempt is made to prevent superheating. However, for accurate work two set-ups must be used, so that one, with solvent only, will give the change of boiling point with any change in pressure. No attempt is made to measure the actual volume of solvent during the experiment. Both methods require 5 ml. of solvent and 20–30 mg. of material.

Determination of Molecular Weight by the Method of Rast.—The method of Rast [108] is very simple. Camphor possesses exceptional solvent power for compounds and gives a high molecular depression of the melting point. One mole of substance in 1 kg. of camphor as solvent gives a melting point depression of 40° C. The method cannot, of course, be used for those substances which are insoluble in camphor or decompose below 170° C. The method really only involves the taking of a melting point. The melting point of the camphor is first taken and then a substance of known molecular weight is added and the depression of the melting point noted. By this means the camphor is standardized for further determinations.

A conical capillary, Fig. 442–1, 40 mm. long, 3 to 5 mm. at the top, and 2 to 4 mm. at the bottom, is weighed exactly on the balance. The sample finely ground is picked up by pressing a small capillary into the material. This small capillary with a bore of 2 mm. and 50 mm. long is wiped free of material adhering to the outside and placed in a large capillary. A fine solid rod, which fits into the small capillary, is inserted and forces out the sample into the bottom of the large capillary. When a sample 0.2 to 0.3 mg. has been added, the large capillary is again weighed which gives the exact weight of the sample. The camphor is introduced in the same manner except that a larger capillary may be used for introducing the camphor. When about 10 times the weight of sample has been added, the large capillary is weighed the third time and this gives the weight of the camphor added. The capillary, Fig. 442–2, is now sealed 20 mm. from the bottom and drawn out to a fine thread 4 cm. long. The capillary, Fig. 442–3, is next dipped into a heating bath, such as concentrated sulfuric acid so that the material is melted and mixed together. The capillary is now attached to a melting point thermometer and placed in a melting point

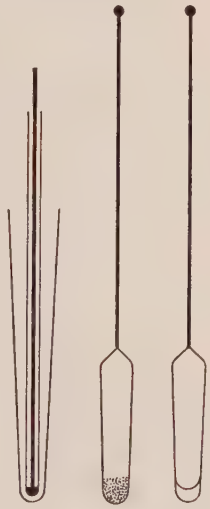

Fig. 442.

[107] Chem. Ztg., **51**, 568 (1927) and A. Rieche, Mikrochemie, **12**, 129 (1932).
[108] Ber., **55**, 1051 and 3727 (1922).

apparatus. The melting point is then determined with the aid of a lens. The capillary is cooled and a second reading taken to check the first.

Calculation:

$$M = \frac{1000\ S.K.}{L\Delta},$$

S = weight of substance,
K = molecular freezing point depression of the camphor used,
L = weight of camphor in mg.,
Δ = observed depressing of the freezing point.

NOTES.—(1) It often happens that a larger sample may be used and thus a larger capillary can be employed. It will be found much easier to charge a large rather than small one such as is described above. It is also much easier to add camphor to a larger capillary.

(2) For those who find that they have a great number of determinations to carry out by this method, the apparatus described by Carl Tiedcke [109] may be of interest. It gives greater convenience in holding the thermometer and capillary, together with a novel container for the sulfuric acid. It consists of a 250 ml. flask with ground-glass top into which is inserted a thermometer. The flask is provided with a stirrer and platinum hook to hold the capillary.

(3) Joseph Pirsch [110] suggests Bornylamine (m.p. 164° C.; mol. m.p. depression E = 40.6) and Camphene dibromide (E = 115), as also suitable for the determination of molecular weight.

For Liquids—Micro Victor Meyer Method.—The principle of the method consists in vaporizing the liquid under controlled conditions and indirectly measuring the volume by observing the change in pressure. The method [111] is simple, and the entire determination takes about 20 minutes. Another form of the micro Victor Meyer apparatus was developed by Lakshminarayan and Nayak.[112] The average error is about $\pm 2.0\%$.

Methods based on the Victor Meyer principle,[113] but which vaporize in a system initially filled with mercury, are not as simple to carry out as the above method. The volume is determined by weighing the mercury displaced by the vaporized sample.

Apparatus.—The construction of the apparatus [111] is simple. The details are given in Fig. 443. It is essentially an inner jacket A, fitted with a mercury manometer; the inner jacket is surrounded by an outer jacket B, to maintain constant temperature during the vaporization. A and B are constructed from a 15×150 mm. and a 25×200 mm. Pyrex test tube respectively. On the bottom of A is sealed a tube 40 mm. long and 4 mm. in diameter, and three short lengths of rod are sealed at C equidistant around the circumference so that A is centered in the jacket B.

The Pyrex stopcock at D should have a bore not less than 2 mm. E is a capillary tube of 0.5 mm. bore. A 100 mm. length of 5 mm. tubing is sealed to the capillary tubing at F. G is a trap to catch any air rising from the manometer. J is a water condenser. A reference mark for the mercury

[109] Mikrochemie, **18**, 223 (1935).
[110] Ber., **65B**, 1227–9 (1932).
[111] Bratton and Lochte, Ind. Eng. Chem., Anal. Ed., **4**, 365–7 (1932).
[112] J. Indian Chem. Soc., **8**, 599–603 (1931).
[113] Niederl, Trautz and Plentl, Ind. Eng. Chem., Anal. Ed., **8**, 252 (1936).

manometer is etched just below the seal *F*. Before use the inner jacker *A* is filled with water to the reference mark to determine its volume. *N* is an asbestos board with a hole to admit the jacket *B*. *A* is supported in the outer jacket *B* by a split stopper. *H* is a 300 mm. reference scale. Determinations may be carried out under reduced pressure by attaching the rubber connection *K* to *A* and applying suction.

Determination.—The liquid, 2–10 mg., is weighed in the usual manner into a capillary of such diameter that it will readily pass through the bore of the stopcock *D*. The form is shown in Fig. 444–*A*. The upper end of the constric-

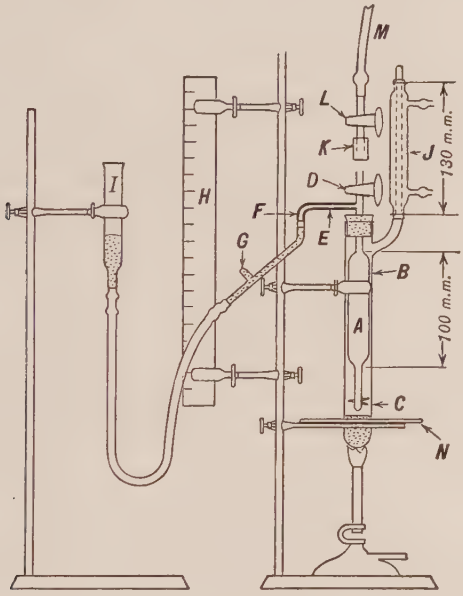

Fig. 443.

tion is closed and a bead formed, Fig. 444–*B*, which is larger than the bore of the stopcock. A liquid with a boiling point 15–20° C. above that of the sample is poured into *B* to a depth 10 mm. below the end of the inner jacket *A*. The manometer is filled with mercury and *A* tilted to fill trap *G*. It is then placed inside of *B*, stopcock *D* is closed, and the burner under *B* is lighted. The liquid is boiled just vigorously enough so that *B* is filled with vapor at all times. The level of the mercury in the right hand manometer is brought to the reference mark and *D* is closed. When no change in mercury level is noted when *D* is closed, the determination is begun.

Stopcock *D* is opened and the capillary inserted, the bead of which rests on the bore of the stopcock. The mercury is brought to the reference mark and the level of the mercury in *I* is read on the scale *H* to 0.2 mm. *D* is closed, thus breaking the capillary and it falls to the bottom of *A*. The levelling bulb is gradually raised and when no further increase in pressure in *A* is noted, the

mercury is adjusted to the reference mark and the level read. The difference in the initial and final readings gives the change in pressure in A. I is lowered, the plug from the broken capillary removed from D and a long capillary inserted into A, and the vapor removed by suction. By making the long capillary slightly smaller than the sample capillary the latter may be retained on the end of the long capillary, when suction is applied, and thus is removed from the apparatus.

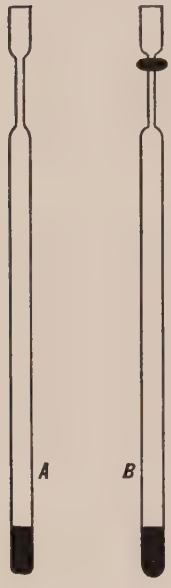

Fig. 444.

Those compounds which tend to decompose when heated to their boiling points at atmospheric can be vaporized at reduced pressure as follows: The sample tube is inserted in D and L is connected to D by the rubber pressure tubing K. L is closed, and M is connected to a vacuum line. I is lowered so that the mercury at F falls to a point just above G. L is slowly opened and if necessary I is again lowered. L is then closed and the mercury brought to the reference mark. If the mercury level remains constant, the level of the mercury is recorded in mm., the sample tube broken by turning D and the determination completed as previously described.

Calculation:

$$\text{M.W.} = \frac{22410 \times 760 \times T \times W}{1000 \times 273 \times V \times \Delta p},$$

where T = absolute temperature of the vapor bath,
W = weight of sample taken in mg.,
V = volume of inner jacket in ml.,
Δp = change of pressure within A in mm.

Collecting Constants.

$$\text{M.W.} = K \times \frac{T \times W}{\Delta p}.$$

The constant K for any apparatus can be calculated when the volume of the inner jacket is known.

Notes.—(1) The following minor changes will be found to make the apparatus more convenient:

(*a*) The tube I should be made of tubing 6–7 mm. inside diameter with a funnel made of tubing 15 mm. × 100 mm. sealed on. It is easier to read the mercury on the scale when it is contained in a smaller tube.

(*b*) The tube beginning at F should not have as steep an angle, as there is considerable strain on this tube with the weight of mercury.

(*c*) A vacuum jacket beginning at the point C and extending up to the bottom of the water condenser will prevent excessive condensation and maintain a more uniform temperature in A.

(*d*) If the apparatus is in constant use, a thermometer well is useful so that the tube A need not be removed to get the temperature of the boiling liquid

(2) If air causes decomposition of the sample, jacket A may be filled with an inert gas.

(3) Bath liquids which can be used are: water, B.P. 100° C., p-cymene, B.P. 180° C., alpha-naphthyl methyl ether, B.P. 269° C., benzyl benzoate, B.P. 319° C.

GAS ANALYSIS

The apparatus described is designed for carrying out a gas analysis using 25 to 100 cu. mm. The degree of precision is of the same order of magnitude as that ordinarily attained in macro gas analysis.[114]

Apparatus.—Fig. 445 is a diagram (Blacet et al.) drawn to scale of the apparatus. *A* is a water jacketed microburette. This is a capillary tube of approximately 0.5 mm. in diameter and graduated to read in cu. mm. with the zero mark at the top of the scale. The total capacity is about 112 cu. mm. The upper end is bent as shown and ends in a capillary of small external diameter to facilitate the intake and discharge of gases. The tip of this capillary is ground and fire polished to a radius of curvature somewhat less than that of the top of the gas holders *H* and *J*. The lower end of the burette is sealed to a larger tube containing a trap to insure the exclusion from the capillary of impurities and chance solid material which may be introduced in the sealing process. The device represented by *P*, *R*, *S*, and *B* is used to move the mercury and gas sample up and down the microburette. *P* is an iron cylinder into which the bell-shaped lower end of the burette is cemented by the sealing wax *N*. The wax is also used here to close the water jacket of the burette. *R* represents an elastic rubber cap. The lower flange of this cap is firmly secured against the lower edge of *P* in a manner which may be deduced from a study of the drawing. *S* is a metal plunger which is attached by a swivel to the screw *B*. The space above *R* is filled with mercury. By manipulating *B* the plunger is forced either up or down causing a flow of mercury or of gas through the capillary burette *A*. Since *P* is the only one of the metal parts which comes in contact with the mercury, it is the only one which must be made of some non-analgamating material. By means of telescoped brass tubes *C* and *D* and the machined screw *E*, everything on the table *F* can be moved up or down with perfect control. *G* is a mercury reservoir of 7 cm. diameter. *H* and *J* are the containers for the gas samples and are also used

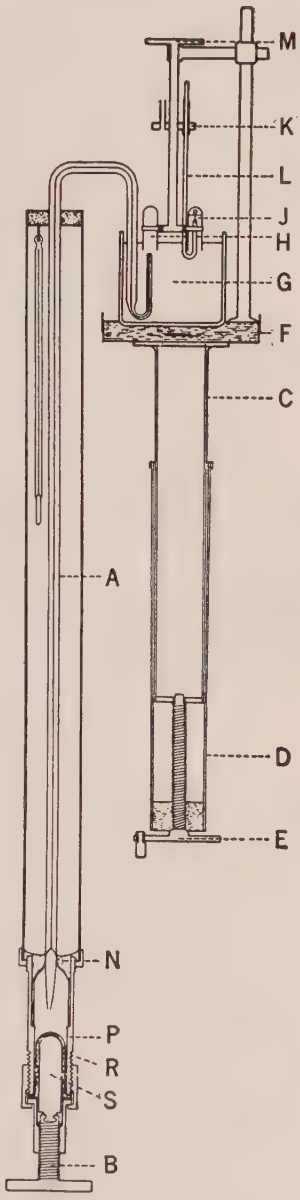

FIG. 445.

[114] Blacet et al., Ind. Eng. Chem., Anal. Ed., 3, 266 (1931); 5, 272 (1933); 6, 334 (1934); 9, 44 (1937). Swearingen, Gerbes and Ellis, Ind. Eng. Chem., Anal. Ed., 5, 369 (1933); Seevers and Stormont, Ind. Eng. Chem., Anal. Ed., 9, 39 (1937).

in the processes of absorption and explosion as will be explained later. They have a capacity of approximately 2 ml. each. In the diagram only two are shown but in fact 4 of them are symetrically attached by means of circular steel springs to the revolving table *M* (see Fig. 445). *K*, the absorbent holder guides, are attached directly on the shaft which supports the gas holders *H* and *J* and are made of a brass tube which acts as a guide for placing and supporting the absorbent holder *L*. Since there are 4 absorbent holders, several separate analyses may be in progress at one time. A rubber band made by cutting a short length from a suitable rubber tube prevents the absorbent holder *L* from extending too far into the gas sample. In Fig. 445, *K* and *J* are shown projected on a vertical plane. Their relative positions are shown more clearly in Fig. 446, in which the spider supporting the 4 guides is shown properly oriented above the one which supports the gas holders. The gas holders are held in position by steel ribbon springs. The apparatus may be purchased from Eimer and Amend, New York City.

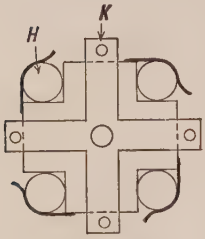

Fig. 446.

Collection and Storage of Samples.—It is not always possible to collect the gas sample directly in the analytical apparatus. For transportation of such samples, the following apparatus is used. A circular iron penumatic trough, 2 cm. in diameter and 1 cm. in depth, which can be lowered into the mercury reservoir of the apparatus, Fig. 445, is welded to an adjustable iron arm of a small ringstand. A second adjustable arm carries a steel spring clamp into which the gas holders can be slipped by a horizontal movement. This device makes it possible to take a small sample of gas to or from the main apparatus without danger of loss or contamination.

Storage of samples may be accomplished by having a metal clip, Fig. 447, made to fit around the gas holder and this in turn fit on the rim of a mercury reservoir.

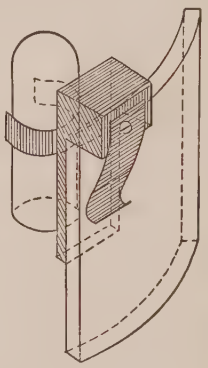
Fig. 447.

The apparatus described above has been modified by Swearingen, Gerbes and Ellis, and later these modifications incorporated into an apparatus by Seevers and Stormont. The design is primarily for rapid and accurate work on a large number of samples. The use of a horizontal gas burette eliminates the tedious raising and lowering of the mercury column. The apparatus as described by Seevers and Stormont follows:

The details of the microburet, drawn to scale, are shown in Fig. 448. The whole unit is rotated around the horizontal axis of the capillary on the bearings, *NN*, by the lever, *P*. The unit may be easily removed from the bearings, for cleaning the buret, by release of the thumbscrews. The extent of rotation of the unit is limited by the adjustable stop *H* to prevent damage to the capillary arm. This arm is further protected by the support *I*.

The microburet is of 0.66 mm. capillary Pyrex tubing, fused to a 2 mm. capillary at the manipulator end to prevent the accidental aspiration of the sample into the manipulator reservoir. The portion of the capillary used for

volume measurements has a capacity of 0.18 ml. and is enclosed in an ordinary 50 ml. buret with scale divisions which completely encircle the buret to prevent parallax. Both capillary and reading buret are further enclosed in a heavy glass water jacket which fits snugly into a rigid brass tube, threaded at both ends for the brass end caps and cut away on both sides, as indicated, to allow for reading of the buret. The glass parts are thus held rigidly in place between two rubber gaskets when the end plate nearest the buret tip is screwed into place. Manipulation of the thumbscrew *R* results in pressure on the 18-gage Allegheny metal diaphragm *L* and activation of the mercury thread. The metal diaphragm is much superior to any of the numerous contrivances which the authors have utilized to activate the mercury thread, since there are no parts to replace and hysteresis is reduced to a minimum.

The manipulator reservoir is machined from a steel block, open at the end to receive the plate *T* which may be conveniently removed to allow for cleaning of the capillary. A thin cardpaper gasket, saturated with de Khotinsky wax,

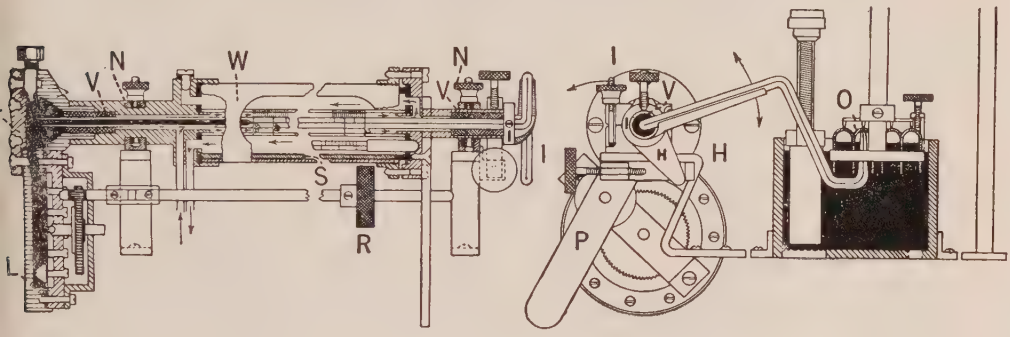

Fig. 448.

and sealed into place after warming the metal parts, effects a mercury-tight union of both the end plate and the diaphragm with the reservoir. In assembling, the capillary tube is inserted through the unit and spaces *VV* are filled with sealing wax over a rubber gasket. Mercury is introduced into the apparatus through the opening at the top of the manipulator reservoir and sealed with a tight-fitting needle valve. As indicated by the arrows in the diagram, water from a constant-temperature bath circulates by gravity feed between the capillary and the reading buret and returns to the outlet through the space between the reading buret and the outer jacket. It empties into a reservoir from which it is elevated to the bath by a water pump. Forced pumping through the apparatus results in so much bubbling as to make reading difficult.

The relation of the microburet to the absorption reservoir is shown in Fig. 449.

By rotation of the buret unit around its horizontal axis, the buret tip may be introduced into any capsule of either the sample carrier *N* or the capsule holder *Q*, since the latter two have not only a vertical axis of rotation, but are free to describe an arc around their respective supporting rods.

Absorption of the various constituents is accomplished in the four capsules in the holder *Q*, which is shaped like a segment of a circle to allow vertical passage of the bead holders when the capsules are turned toward the buret tip. The four capsules are held in the same horizontal plane by the stops *A*. The capsules in this holder, as in the carrier, are held firmly in place by a coiled spring and ball bearing *W*. The authors have found this to be a most satisfactory method of holding the capsules firmly and still allowing for easy

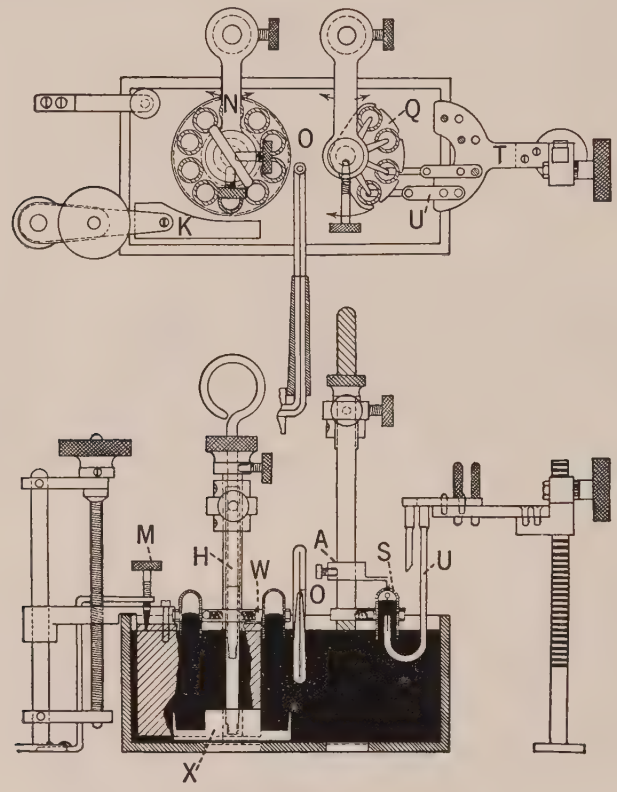

Fig. 449.

removal. Steel forceps made from a sponge clamp are used to handle the capsules, which are filled by slowly inverting under mercury before insertion into the holder. Care must be exercised to prevent small air bubbles from adhering to the walls of the capsule during this procedure.

The interchangeable bead holders are of glass tubing fastened into the metal shank with wax, or preferably an adjustable rod of stainless steel fastened to the bead-holder arm by means of a set screw. The platinum tip is of sufficient length that the glass portion of the holder does not enter the sample. The bead holders are of uniform size and shape and held in fixed position by two pins upon the cross arm *T* (Fig. 449) which is raised or lowered by the rack and

pinion. It is thus possible to insert four beads into the absorption capsules without any bead coming in contact with the inner surface of the capsules. As reported repeatedly, such an occurrence ruins the analysis. The level of the mercury in the reservoir may be changed by raising or lowering the Bakelite block *K*. This provision is necessary in order to maintain a constant level of mercury in the reservoir, and is shown by the ivory tipped indicator at *M*.

Preparation of Samples.—All samples must be dried before analysis and the burette must also be kept free from moisture. It has been found that the normal vapor pressure of water does not exist in such small gas volumes. The dry wall of the burette absorbs moisture and erratic results are thus obtained in the analysis of samples containing moisture.

The Preparation of Beads.—(1) Beads of solid reagent are prepared unless otherwise stated, by melting the material and taking it up in a small loop of platinum wire. The platinum wire is sealed into a glass holder as shown in Fig. 445.

(2) Beads for liquid reagents are made by taking soft glass 100–150 mesh and heating it carefully until it just begins to fuse. It is shaped to a sphere of approximately 2 mm. diameter. This is then attached to a straight platinum wire by heating the wire and letting the end of it become embedded in the bead. The pores of the bead are filled when it is dipped into a liquid reagent.

Swearingen, Gerbes and Ellis made a bead for liquid reagents by taking a mixture of 70% grog and 30% kaolin. The grog, ground porous earthenware, is sifted to a uniform size, passing 120 and retained by 140 mesh screen. The kaolin should pass 200 mesh. The consistency of the mixture should be such as to allow it to be dipped up with the platinum wire loop in order to get a smooth surface. The bead is baked in a flame for a few minutes and is then ready for use.

Operation of Apparatus.—The operation of the apparatus, Fig. 445, as described by the authors is given below taking the determination of oxygen in dry air as an example.

Specific Determinations: *Oxygen.*—First the containers *H* and *J* are filled with mercury. This is done by placing a glass tube, which has been drawn out to a capillary and properly bent, so that its end will go down into the reservoir *G* and up to the top on the inside of the containers. If the containers are clean and have a top of smooth curvature all the air can be drawn out with ease. The high surface tension of mercury facilitates this. Several hundred cubic millimeters of the air are introduced into *H*. This constitutes the sample for analysis upon which several determinations presumably are to be made. If a Toepler pump is used for the purpose of introducing samples, its outlet is bent in the same manner as the tip of the buret and placed permanently in position in the reservoir and at the same height as the buret tip. The rotating table *M* is mounted on an adjustable arm so that the containers can not only rotate completely around the central shaft but may be moved to any desired position within the reservoir. Accordingly, the outlet for the Toepler pump may be at the back side of the reservoir and a container can be moved over its tip and filled.

The next step is to obtain a known volume for analysis. By means of the screw *B* all of the air in the buret is replaced by mercury. The tip must be under the surface of the mercury in *G* while this is done, otherwise when it is

submerged it will invariably carry a small air bubble with it. *H* is now placed directly over the tip, and by lowering the table *F*, the tip is brought into the gas sample. By means of *B* a portion of the sample is drawn into the buret. The volume ordinarily taken varies from 25 to 100 cu. mm. depending upon the total amount available and the subsequent treatment to which it is to be subjected. The table is then raised so that the level of the mercury in the reservoir is on the level with the uppermost calibration mark in the water-jacketed part of the buret. By further unscrewing *B*, the gas, followed by a thread of mercury, is brought into the calibrated portion for measurement of its volume. When its upper level is at the same height as the surface of the mercury in the reservoir, it is then theoretically under atmospheric pressure. However, the apparent pressure in the buret may be considerably in error, owing to the fact that mercury has a tendency to stick to clean dry glass. If no precautions are taken two subsequent volumes on the same gas sample may be obtained which vary as much as 1% from one another. To reduce this source of error two expedients are used. First, the buret is gently tapped with the finger as the gas is being brought to the desired position. Second, five independent readings are always recorded and the average taken in calculating the volume. These precautions reduce the probable error in all cases below 0.2%.

After the volume readings for the run have been recorded along with temperature and barometric readings, container *J* is brought over the buret tip and the gas in the buret expelled into it. The gas is now ready to have the oxygen absorber introduced. The removable holder *L* has a platinum loop sealed in its tip. In this loop is fused a small bead of yellow phosphorus. The fusion may ordinarily be done by placing a fresh piece of phosphorus in the loop by means of forceps and then holding it over a warm resistance coil or even in the sunlight. By quickly removing when fusion occurs and placing it under the mercury, spontaneous combustion may be avoided. In any case it should not be allowed to remain in the air any length of time, for the moisture of the air along with oxygen causes a film of phosphoric acid to coat the bead, thus making it a much slower absorber. As shown in Fig. 445, the holder is placed in the guide *K*. The container *J* is brought into position and the phosphorus introduced into it. In this operation care must be taken not to allow the glass of the holder *L* to touch the walls of the container. It has been found that a cold tube introduced into mercury in this way is coated with a film of air, part of which will be imparted to the walls of *J* if contact is made between the two glass surfaces. On this account the guide is necessary for the introduction of the absorber up the center of the container. The height of *K* is also arranged so that only the phosphorus bead and a little platinum wire enters the gas bubble.

Fifteen minutes has been found sufficient time to allow for complete absorption in practically all cases. However, absorption to constant volume is practiced. After absorption has occurred and the absorbent removed, the tip of the buret is brought to the top of the container (more accurately, the top of the container is brought to the buret tip) and the residual gas taken into the buret. With the proper manipulation of *B*, *E* and *M* this operation presents no practical difficulties. If the entire gas bubble is not drawn into the buret intact the first time, it need only be driven back into the container and the process repeated. The experimenter soon acquires skill in this regard. The volume of the residual gas is now measured and the temperature and the

barometric pressure again recorded. The absorption process is repeated for 5 minutes more, and if no further reduction in volume occurs, all data necessary for the simple standard method of calculation of the determination are complete.

NOTES.—(1) The bead of yellow phosphorus as prepared by Swearingen, Gerbes and Ellis [115] gives very rapid absorption. The presence of moisture gives a film of phosphoric acid. To remove this, the bead is washed in water, then alcohol and then dried in a stream of natural gas

(2) The operation of the apparatus of Seevers and Stormont differs only slightly from that outlined above, and such variation may be seen from a study of the drawings, Fig. 448 and Fig. 449.

Water Vapor.—A bead of fused phosphorus pentoxide is used. It is prepared over a glowing electric coil. A flame should not be used because of the moisture generated by it.

Carbon Monoxide.—Specially prepared dry silver oxide is used. It is prepared by means of a strong base and thoroughly washed by decantation. While still somewhat moist the solid is compressed into pellets by applying a pressure of 6000 lbs. per square inch. The pellets are allowed to dry at room temperature. They should not be unduly exposed to air as they take up carbon dioxide. The tip of a straight platinum wire is dipped in a concentrated solution of sodium silicate and then touched to a piece of regular shaped silver oxide 1.5 mm. in diameter. The cement is dry in 10 minutes. Absorption of the carbon monoxide is complete in 10 minutes. No volatile products are formed, so no follow-up absorbent is required.

Ethylene.—The sintered glass bead is dipped slowly into fuming sulfuric acid. The space in the bead becomes filled with liquid and the air is forced out. The bead is wiped with a piece of filter paper to remove excess acid from the exterior surface, and then introduced in the usual way into the gas sample. After 2 minutes the acid is removed and a slightly moist potassium hydroxide bead is added to take up the sulfur trioxide vapor. This absorption is also very rapid. After another 2 minutes the bead is removed and the decrease in volume of the sample due to the presence of unsaturated hydrocarbons is measured.

Acetylene.—A stiff paste is made by moistening cuprous chloride with a dilute potassium hydroxide solution. This is molded in the platinum loop and heated gently until dry, care being taken not to heat the solid until it turns dark in color. This bead gives complete absorption of the acetylene contained in an average sample in 5 minutes. The copper acetylide formed becomes an integral part of the solid bead and does not contaminate the mercury as it is being removed from the reacting system. The potassium hydroxide takes up all of the hydrogen chloride or water vapor formed, so that the decrease in volume gives directly the amount of acetylene which is present.

Hydrogen Chloride, Sulfur Dioxide, Sulfur Trioxide, Hydrogen Cyanide, Carbon Dioxide.—(1) May be absorbed by using a bead of fused potassium hydroxide which, before use, is allowed to absorb moisture from the air.

(2) Or, by using a sintered glass bead and a concentrated solution of potassium hydroxide. The water vapor pressure over this absorbent is negligible. 2 minutes are required for either method.

[115] Ind. Eng. Chem., Anal. Ed., **5**, 369–70 (1933).

Ammonia.—(1) By means of a moistened phosphorus pentoxide bead.

(2) By a sintered glass bead using concentrated sulfuric acid. The absorption is rapid. The results are high by 0.25% from theory.

(3) By means of a potassium bisulfate bead. After dipping the loop in the molten bisulfate, the bead is moistened with water and dried in order to leave a surface coated with many fine crystals.

Nitrogen—Inert Gases.—All such gases are determined by difference.

Acetaldehyde and Vapors of Similar Compounds.—A solid potassium hydroxide bead is used. This polymerizes the aldehyde to a resin-like substance which adheres to the bead.

The Determination of Combustible Gases.—Only fair results with small samples are obtained by analyzing such gases using the familiar explosion method. For this method to operate, the mixture must be adjusted rather critically. Blacet and Volman [116] have developed a method whereby the reaction is carried out on a hot surface placed in the system. This was accomplished by a platinum loop shown in the operating position, Fig. 450.

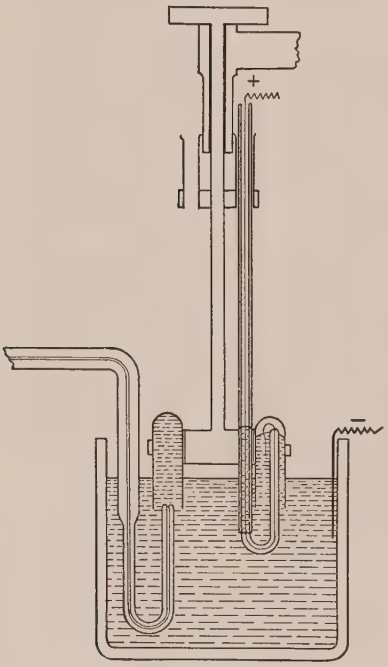

Fig. 450.

The mounting for the platinum is made from a piece of soft glass tubing of the same length and diameter as an absorbent holder. A 7 cm. length of 24-gage platinum wire was placed in the tube in such a manner that about 1 cm. of it extends beyond one end of the tube. Starting at this end, a narrow portion of the tubing is heated carefully, so that a fusion of glass to platinum occurred. By slowly moving the tube through the flame the platinum wire is encased in glass for a length of about 5 cm. It is important that no air bubbles be trapped in this process. The glass and wire are then bent to assume the shape shown in the diagram.

The exposed platinum is bent so that the top of the loop is about 1 mm. above the end of the glass and the tip of the loop can be immersed in the mercury within the gas holder. The top of the loop is worked down for a distance of 1 mm. by careful filing and the use of Crocus cloth, until the cross section is approximately one-third of the original. By placing a small amount of mercury in the unconstricted portion of the mounting, electrical contacts can be made, as indicated. The large mercury reservoir serves to complete the circuit.

In the use of this combustion coil, it is found convenient to have available an electrical potential of about 10 volts and to regulate the glow of the coil by means of a slide wire rheostat placed in the circuit.

[116] Ind. Eng. Chem., Anal. Ed., **9**, 44–5 (1937).

Nitrous Oxide.—A measured volume of pure hydrogen is added to the sample and the combustion coil placed in position as shown in Fig. 450. After adjusting the coil so that a small amount of the glass insulation appears above the mercury surface, the current is turned on and regulated until the thin portion of the platinum wire appears reddish orange in color. Complete reduction takes place in 4 minutes. The coil is removed and a bead of fused potassium hydroxide introduced to remove the water vapor. The volume decrease is a direct measure of the amount of nitrous oxide originally present.

Methane.—The procedure is the same as above except oxygen or carbon dioxide free air is introduced. After the water vapor has been removed the carbon dioxide produced is determined in the usual way and represents the amount of methane in the original sample.

Hydrogen-Oxygen.—Hydrogen may be determined by the use of oxygen and vice versa, by using the combustion method described above.

A bead made by fusing together cupric oxide and potassium hydroxide can also be used for the rapid and complete absorption of hydrogen. The reagent is prepared by first fusing the oxide in the platinum loop and then touching the molten mass to an approximately equal amount of the solid hydroxide. The two substances coalesce and, after cooling, a smooth dark blue bead results. By heating the gas sample in the presence of this solid, hydrogen is rapidly oxidized and the water formed in the reaction is absorbed at the same time. The decrease in volume represents directly the amount of hydrogen in the sample. The total absorption time will not exceed 15 minutes.

NOTE.—The method of surface combustion cannot be used if the time for the reaction to go to completion causes oxidation of the mercury. There is some evidence for this at the end of 15 minutes.

Key References to Additional Applications and Methods

References are given below to micromethods and determinations which will be of value to those working on special problems. Bibliographies, together with brief details of the procedures on specific determinations, appear frequently in the volumes of Mikrochemie and Mikrochimica Acta.

Applications of Microanalysis

1. *Applications of Microanalysis to Agricultural Industries.* de Saint-Rat IV Congr. intern. tech. chim. ind. agr. Bruxelles, **2**, 80–101 (1935).

2. *The application of microanalysis to the analysis of commercial products* is carefully reviewed by Edmund Grundsteidl (Mikrochemie, **16**, 247–320 (1934)). Papers are reviewed which appeared from 1918 to 1928.

Mikrochemie beginning volume 14 (1933–34) reviews the microchemical literature for the preceding year and has a section on technical analysis. This supplement appears regularly with each volume.

3. *Mineral Analyses.* Microanalysis of Silicates.—Determination of Iron, Aluminum, Magnesium, Calcium, Titanium and Manganese (Preliminary announcement). Karl Schoklitsch, Mikrochemie, **20**, 247–53 (1936).

Microanalysis of Monazite.—A method for the analysis of small quantities of monazite. Hecht and Kroupa, Z. anal. Chem., **102**, 81–99 (1935).

4. *Microchemical Analysis of Steel.* Determination of Manganese. Andre Leroy. Bull. Soc. Chim. (5), **3**, 1125–6 (1936).

5. *Photometric Microanalysis of Water.*—C. Urbach, Mikrochemie, **10**, 483–504 (1931–32); **11**, 37–60 (1932); **13**, 31–54, 201–224 (1933).

Special Methods of Analysis

1. *Quantitative Analysis of Unweighable Amounts of Material.* F. Emich, Mikrochemie, **13**, 283–288 (1933). Suggestions are made as to the use of an "enlargement" process whereby the final factor for calculation may be increased. Several examples together with possible methods are given.

2. *The Heyrovsky Polarograph.* The principle is not new but the design of the apparatus and method of analysis was developed by J. Heyrovsky of Charles University, Prague.

By using a dropping mercury cathode and by constantly increasing the voltage to a sample in solution, a point is reached, characteristic for each reducible compound, where the intensity of the current suddenly increases. The intensity varies with the concentration of the substance. Only a few drops of solution are required and the sample is not destroyed by the analysis. While the method is not recommended as a routine procedure of general application it has been found useful, by workers in this country and abroad, in the study of special problems dealing with the quantitative analysis of traces of metals, and some inorganic and organic radicals. The usual limit of sensitivity is 0.0001 mg. A study of the method has been made at the University of Wisconsin, and numerous references to the method appear in the literature. A booklet, "Chemische Analysen mit dem Polaragraphen" by Dr. Hans Hohn, published by Julius Springer, Berlin (1937) deals with the polarograph and its practical applications in a very thorough manner.

3. *The Use of Fluorescent Analysis in Michrochemistry.* Max Haitinger, Mikrochemie, **16**, 321 (1934–35).

Physical Methods

1. *Microcalorimetry.* Brian Whipp, Phil. Mag., **18**, 745–59 (1934). Determination of Heat of Combustion with the Microbomb. J. J. Vrigling, Chem. Weekblad., **32**, 20–2 (1935). Researches on Calorimetry. Generalization of the Method of Electrical Compensation. Microcalorimetry. A. Tian, J. chim. phys., **30**, 665–708 (1933). A Semimicrocalorimeter for Measuring Heat Capacities at Low Temperatures. Daniel R. Stull, J. Am. Chem. Soc., **59**, 2726–33 (1937).

2. *Density.* Micropycnometer Method for Density Determinations. G. R. Clemo and A. McQuillen, J. Chem. Soc., 1220 (1935). Micro Density Determination of Solids and Liquids. Eugene W. Blank and Mary L. Willard, J. Chem. Ed., **10**, 109–12 (1933).

3. *Distillation.* Microanalytical notes: 1. Some Improvements in Methods of Dealing with Small Quantities of Liquids and Precipitates. B. L. Clarke and H. W. Hermance, Mikrochemie, **18**, 289–298 (1935). This deals with improved methods of filtration, evaporation and distillation. Fractional Distillation of Extremely Small Volumes of Liquids. Benedetti-Pichler and Rachele, Mikrochemie, **19**, 1–5 (1935). Separates 10 cu. mm. into fractions of 2 cu. mm. Microdistillation of Liquids. A Microdistillation Apparatus. Lyman C. Craig, Ind. Eng. Chem., Anal. Ed., **8**, 219–20 (1936). Isolation from Human Tissues of Easily Volatile Organic Liquids and their Identification. A. O. Gettler and H. Siegel, Arch. Path., **19**, 208–12 (1935). Microfractionating Column for Liquids Having Low Heat of Vaporization. Paul E. Weston, Ind. Eng. Chem., Anal. Ed., **5**, 179 (1933).

4. *Extraction.* Micro Fat Extraction. Microextractor. L. Titus and V. W. Meloche, Ind. Eng. Chem., Anal. Ed., **5**, 286–88 (1933).

5. *Microrefractometer.* A microrefractometer (for liquids) and its use in chemical microscopy. E. E. Jelley, J. Roy. Microscop. Soc., **54**, 234–45 (1934).

6. *Viscosity.* Microviscometer. F. M. Lidstone, J. Soc. Chem. Ind., **54**, 189–90 T (1935). Viscosity Determinations with Small Amounts of Material. Otto Merz, Farben. Ztg., **37**, 1192–3 (1932). A Microsaybolt-type Viscometer. Stuart M. Rogers and Linden R. Adkins, Ind. Eng. Chem., **20**, 742 (1928).

Determination of Organic Radicals

1. *Carbonyl Group.* Microdetermination of Carbonyl Groups. F. Frhr. v. Falkenhausen, Z. Anal. Chem., **99**, 241–57 (1935).

2. *Carboxyl.* A Micro Method for the Determination of Carboxyl Groups in Organic Acids. Tsurumi and Sasaki, Science Repts. Tokohu Imp. Univ., 1st Ser., **19**, 681–8 (1930). They employ a micromodification of the macro procedure of Hurter and Edward, J.A.C.S., **35**, 452–61 (1913).

3. *Active Hydrogen.* A. Soltys, Mikrochemie, **20**, 107–125 (1936) (Mikro-Zerewitinoff). P. M. and G. F. Marrian, Biochem. Jr. London, **24**, 746 (1930). H. Roth, Microchemie, **11**, 140 (1932). Micro Determination of Active Hydrogen with Deuterium Oxide. R. J. Williams, J.A.C.S., **58**, 1819–21 (1936).

Fats:

4. *Microdetermination of the Reichert-Meissl-Wollny, Polenkske and New Kirschner Numbers,* H. Vasbinder, Pharm. Weekblad., **71**, 1193–7 (1934).

Methods of Analysis for Specific Compounds or Elements

1. *Aluminum.* A. Benedetti-Pichler, Mikrochem. Pregl Festschr., 9–13 (1929) (gravimetric determination).

2. *Benzene.* A Microcolorimetric Method for the Determination of *Benzene.* Pearce, Schrenk and Yant, Bur. of Mines, Report of Invest. No. 3287 (1935).

3. *Microcolorimetric Determination of Benzene in Blood and Urine.* Pearce, Schrenk and Yant, Bur. of Mines, Rept. of Invest. No. 3302 (1936).

4. *Bismuth.* The Micro-electrolytic Determination of Bismuth and Lead and their Separation by Graded Potentional. A. J. Lindsey, Analyst, **60**, 744–6 (1935). Microdetermination of Bismuth as Bismuthyl Iodide. Hecht and Reissner, Z. Anal. Chem., **103**, 283–8 (1935).

5. *Calcium.* Microdetermination of Calcium in Sea Water. Kirk and Moberg, Ind. Eng. Chem., Anal. Ed., **5**, 95–8 (1933).

6. *Microdetermination of Carbohydrates.* Collected References. I. Z. Dische, Mikrochemie, **10**, 127–187 (1931). Collected References. II. A. Wasitzky, Mikrochemie, **16**, 87–114 (1934–35). The above references bring the subject up to 1934 and also outline the various procedures.

7. *Palladium.* Microanalytical Determination of Palladium by Means of Dimethylglyoxime, Methyl Benzoylglyoxime and Salicylaldioxime. H. Holzer, Z. anal. chem., **95**, 392–400 (1933).

8. *Platinum and Iridium.* Microdetermination of Platinum and Iridium and of Associated Chloride and Potassium. Drew, Treso and Wyatt, J. Chem. Soc., 1787–90 (1934).

9. *Toluene.* A Microcolorimetric Method for the Determination of Toluene. Yant, Pearce, Schrenk, Bur. of Mines, Rept. of Invest. No. 3323; 311 (1936).

10. *Zinc.* Micromethods for the Determination of Zinc. P. L. Hibbard, Ind. Eng. Chem., Anal. Ed., **6**, 423–4 (1934).

METALLOGRAPHY [1]

Metallography is that branch of the science of metallurgy which treats of the constitution and internal structures of metals and their relations to the physical properties. The success of its application to the examination of metals or alloys is dependent to a great extent not only upon a knowledge of their chemical composition, method of manufacture, and mechanical or thermal treatment, but also on the fundamental laws which relate to their fusion and solidification and the internal changes which occur while whole or partly solid.

THE MICROSCOPE

The application of the compound microscope to the study of opaque objects examined by reflected light introduces conditions somewhat different from those where thin transparent sections are used. The fundamental laws pertaining to the manipulation and use of the microscope are, however, applicable in either case.

There are two methods of illumination: (1) *normal* or *vertical* illumination in which the light is directed on to the specimen at right angles to its surface; (2) *oblique* illumination in which the light is directed obliquely to the specimen from a source outside the lenses of the instrument. Fig. 451 is a sketch showing the two methods.

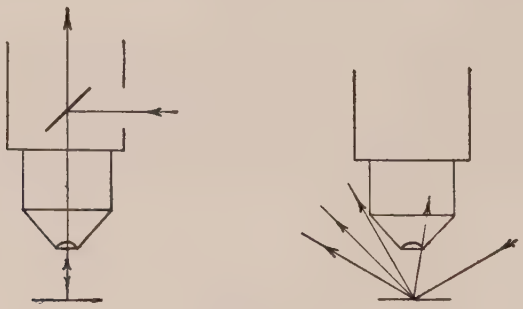

Fig. 451.

Oblique illumination is the simplest because no special attachments to the microscope are necessary, but it is valuable only when low magnifications are used and where it is a question of examining small differences in level on the polished and etched surface. Vertical illumination is the method more

[1] Chapter by Joseph Winlock, Chief Metallurgist, Edward G. Budd Manufacturing Co.

commonly used. In this system the light enters the instrument through an aperture in the side of the tube and strikes a disc of glass set at an angle of 45 degrees which reflects the light downward to the specimen. The light reflected by the surface of the specimen then passes upward through the disc and forms the image. If desired, a totally reflecting prism may be used instead of the plain glass disc.[2]

The choice of lenses depends upon the character of the metal and upon the magnification desired, but for ordinary work the following types [3] are suggested as being suitable:

(*a*) For magnifications from 0 to 10: a photographic lens of approximately 72 mm. focal length to be used without ocular.

(*b*) For magnifications from 10 to 30: a photographic lens of approximately 35 mm. focal length to be used without ocular.

(*c*) For magnifications from 30 to 75: an achromatic [4] objective of approximately 32 mm. focal length with Huyghens ocular (approximately ×5).

(*d*) For magnifications from 75 to 150: an achromatic objective of approximately 16 mm. focal length with Huyghens ocular (approximately ×5).

(*e*) For magnifications from 150 to 1000: an apochromatic [5] objective of approximately 4 mm. focal length with an ocular compensated for apochromatic objectives.

The magnifications in microphotography should be accurately determined by measuring the image of a stage micrometer scale and not by calculations from lens combinations and projection distances.

In order to overcome slight degrees of chromatic aberration even in apochromatic objectives, the use of monochromatic light is preferable and for this purpose the light before reaching the specimen should be allowed to pass through a colored glass screen. Filters having a dominant wave-length of 5500 Å. U. (i.e., yellowish green) are very satisfactory for general use. In very high magnification a violet or blue filter is recommended.

[2] A slight degree of oblique illumination may be obtained by rotating the reflector of the vertical illuminator.

[3] It should be borne in mind that increasing the magnification by increasing the bellows length of the camera adds nothing to the detail of micrograph. This depends for the most part upon the resolving power of the objective used. See also Patterson, W. L., Trans. A. S. S. T., Vol. 11, No. 2, Sept., 1921.

[4] Achromatic lenses are those corrected for two colors.

[5] Apochromatic lenses are those corrected for three colors.

PHOTOGRAPHIC MATERIALS

A medium speed, moderately fine-grained orthochromatic photographic plate such as Eastman's Wratten and Wainwright Metallographic Plates should be used. In order to bring out the details of the structure, a printing paper with a glossy surface should be used, e.g., Eastman's Regular Glossy Velox. The maximum degree of gloss may be obtained by drying the prints on "ferrotype" plates which have been previously wiped with a solution of paraffin in benzol and then polished with a clean dry cloth.

Complete directions regarding the process of developing and printing are furnished with each box of plates and paper and for the best results should be rigorously adhered to.

Full information regarding magnification, type and kind of ocular and objective used should accompany each photomicrograph.

PREPARATION OF SPECIMENS FOR MICROSCOPICAL EXAMINATION

The sample chosen for microscopical examination should be as characteristic of the specimen it represents as is a sample for chemical analysis—the size and location depending upon the nature of the article to be examined. Samples of rolled objects, for example, are usually taken so that the surface examined is longitudinal to the direction of work. For convenience in handling, a sample from $\frac{1}{2}$ to $\frac{3}{4}$ inch square and $\frac{1}{4}$ of an inch thick is best.

Soft metals may be cut with a hand or power hacksaw and hard material by means of a thin emery disc or broken with a hammer. Great care should be taken at all times to prevent the metal from becoming unduly heated during the cutting operation on account of the change in structure which might result. If the sample is small, such as wire or thin sheets, some sort of mounting device such as a clamp or small container filled with a low melting alloy [6] in which the sample may be imbedded is desirable. If the edge of the sample is to be examined, it is sometimes convenient—particularly with iron and steel—to plate the sample with a thin coating of copper to prevent the edges from becoming rounded during the grinding and polishing operations.

The coarse scratches caused by the saw or emery disc are removed by grinding on a fine grade emery wheel such as alundum grade 80 P revolving at a speed of approximately 1000 r.p.m. From the emery wheel [7] the sample is taken to a canvas-covered disc revolving at a speed of about 400 r.p.m. armed with flour emery suspended in water.

[6] A very satisfactory alloy melting at about 50° C. can be made up as follows: Lead 30 grams, bismuth 50 grams, tin 25 grams, and zinc 3 grams.

[7] Between each grinding or polishing operation the sample should be thoroughly washed in water. Subsequent polishing scratches should always be at 90° to those immediately preceding.

Mechanical polishing is generally much more convenient and satisfactory than hand polishing. For mechanical polishing a disc of any convenient size covered with a fine-grade broadcloth and revolving at about 400 r.p.m. has been found to be suitable. Jeweler's rouge or levigated alumina are the principal powders used. The 6-hour alumina is a rapid polishing powder and is used on steel and hard materials. Two ounces of the powder are taken for 100 ounces of distilled water. The 12-hour alumina is more comparable to jeweler's rouge and is generally preferred. It is particularly useful for the non-ferrous alloys such as brass, bronze, German silver, etc. One ounce of the powder is taken for 100 ounces of distilled water. The 24-hour alumina is very fine and is therefore used only in special cases such as preparing sections for examination under high magnifications or for polishing very soft alloys. Six-tenths of an ounce of the powder are taken for 100 ounces of distilled water. Certain alloys, such as those rich in lead, become tarnished if water is used for polishing in which case the water should be replaced by alcohol or a thin oil.

With hand grinding and polishing, the sample is rubbed on each of the following emery papers in the order given:

1. Rough commercial No. 0.
2. Smooth commercial No. 00.
3. French-Hubert No. 0.
4. French-Hubert No. 00.
5. French-Hubert No. 000.

Final polishing may be conducted on a block of wood covered with broadcloth armed with jeweler's rouge or levigated alumina.

After grinding and polishing, the samples should be carefully washed in alcohol and dried in an air blast or with a soft cloth. They should be kept in a desiccator until ready for microscopical examination.

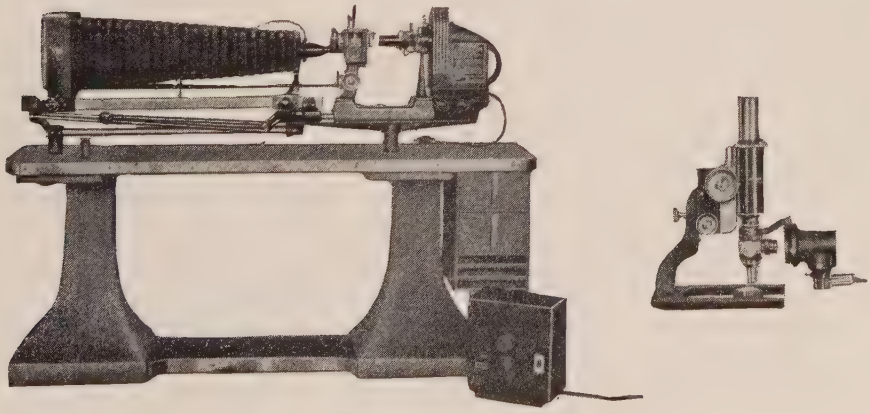

Fig. 452. Equipment for Photomicrograph. (Courtesy of Bausch & Lomb.)

ETCHING SAMPLE FOR EXAMINATION

There are occasions when the sample is examined without etching, e.g., if the metal is thought to contain an excessive amount of dirt, slag, or other non-metallic inclusions. The graphite in gray cast iron or malleable castings or manganese sulfide in steel, etc., may also be seen before the sample has been etched.

In the majority of cases, however, some suitable etching medium is employed to reveal the internal structure by differentially attacking the constituents or crystalline grains of the metal. A few of the more important etching reagents are given in the following list.

Nitric Acid and Alcohol.—A 3% alcoholic solution of nitric acid is used for etching plain carbon, alloy steels and cast iron. The sample is dipped in the solution from two to ten seconds, washed in alcohol and dried in air blast or with soft cloth.

Picric Acid and Alcohol.—A 5% alcoholic solution of picric acid is also used for steels and has been found especially valuable in revealing the structure of pearlite and sorbite.

Concentrated Nitric Acid (sp.gr. 1.42) (after Sauveur).—Used for etching iron and steel. Sample is dipped in acid where it assumes the passive state. Then held in stream of running water causing it to be momentarily vigorously attacked. It is then washed in alcohol and dried.

Sodium Picrate.—Solution made by adding 2 parts of picric acid to 98 parts of a solution containing 25% of caustic soda. Sample is immersed from 4 to 6 minutes in solution heated to boiling, then washed in alcohol and dried. Colors cementite black, leaving ferrite unaffected.

Yatsevitch's Reagent.—Ten milliliters of hydrogen peroxide added to 20 milliliters of a 10% solution of sodium hydrate in water. Sample is immersed from 10 to 20 minutes in solution, washed in alcohol and dried. Reagent should be prepared fresh every day. Used for high-speed steels, coloring the special carbides brown or black.

Le Chatelier No. 1.—200 ml. methyl alcohol, 20 ml. distilled water, 4 ml. hydrochloric acid (sp.gr. 1.18), 2 grams cupric chloride, 8 grams magnesium chloride and 1 gram of picric acid. This solution is used to reveal the macrostructure (structure visible to naked eye) and local segregations, particularly phosphorous. Sample is immersed in reagent until a thin film of copper has been deposited on entire surface. Copper then washed from specimen with a piece of absorbent cotton dipped in ammonia. Sample then washed in water, alcohol and dried. Operation is repeated until structure is plainly visible.

Ferric Chloride (Moore and Gilligan).—40 grams of ferric chloride, 3 grams cupric chloride, 40 ml. hydrochloric acid, and 500 ml. of distilled water. The *modus operandi* is the same as with Le Chatelier No. 1.

Ammonia.—Used for etching copper alloys, gun metal, bell metal, cast bronze, etc. To 5 ml. of ammonia are added a few drops of hydrogen peroxide and applied to sample with a small wad of absorbent cotton.

EQUILIBRIUM DIAGRAMS

The equilibrium diagrams are based on thermal and microscopical data and show the changes observed in many alloys of the same series [8] when passing from the liquid to the solid state (or vice versa) and, if any, those taking place after the metal has completely solidified.

There are three main types of equilibrium diagrams relating to the solidification of metals and alloys, viz., those binary alloys (1) whose component metals are completely soluble in each other when solid; (2) whose component metals are partly soluble in each other when solid; and (3) whose component metals form a definite compound.

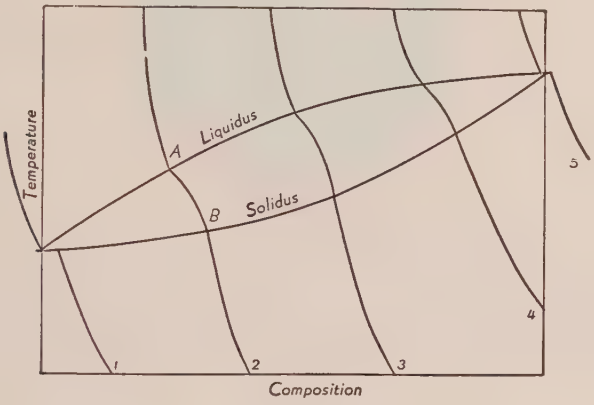

FIG. 453.

Figure 453 [9] shows the equilibrium diagram obtained by plotting several cooling curves of alloys whose component metals are completely soluble in the solid state. It will be noticed that the pure metals at each end of the series solidify at definite temperatures,[10] and not over a temperature range as in the case of an alloy (the portion of curve 2 from *A* to *B*).

[8] With the few exceptions where a pure metal is used, the metals or alloys used in commercial practice are composed chiefly of two elements. The other elements often added to impart special properties and those whose presence is due to the prohibitive cost of removal may be considered separately.

[9] After Sauveur.

[10] "Surfusion" or undercooling may take place if the cooling is slow and undisturbed. Surfusion or superfusion is the unstable condition of a body which, under certain conditions, e.g., slow and undisturbed cooling, may remain liquid after the temperature has fallen below the freezing point.

The appearance under the microscope of alloys of this series is similar to that of a pure metal as in Fig. 454 which shows the structure of almost pure iron magnified 100 diameters. The photomicrograph shows a polygonal network, indicating that the metal itself is composed of irregular polyhedral crystalline grains, each polygon representing a section through a polyhedron. The dissimilarity in shade of the grains is due to the varying orientation of the different grains.

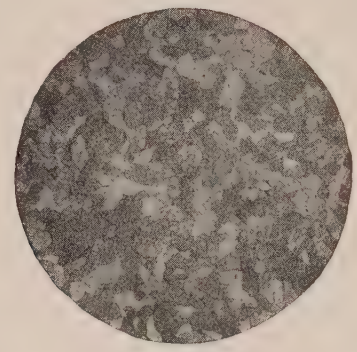

FIG. 454. Photomicrograph of Almost Pure Iron Magnified 100 Diameters, Etched in a 4% Alcoholic Solution of Nitric Acid.

The alloys of which this diagram is typical are those of gold and platinum, copper and nickel, gold and silver, etc.

The equilibrium diagram of alloys whose component metals are partly soluble in the solid state is shown in Fig. 455.

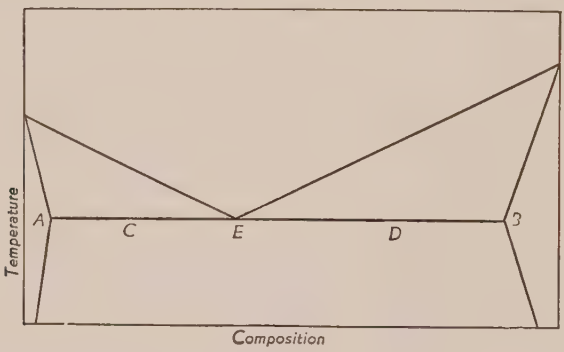

FIG. 455.

The portions at each end of the diagram appear similar to that shown in Fig. 453 of alloys whose component metals are completely soluble in the solid state whereas the middle portions show the diagram typical of those alloys whose component metals form a eutectic. A photomicrograph taken at *C* would appear as in Fig. 456.[11] Here the metal in excess of the eutectic ratio has

[11] After Sauveur.

solidified first, forming the major portion of the alloy with the matrix composed of the eutectic [12] of the two metals which solidifies along the line AB. At E

FIG. 456.

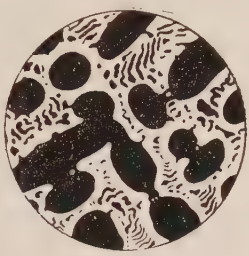

FIG. 457.

FIG. 458.

the structure would be composed entirely of eutectic as shown in Fig. 458. At D the reverse of the conditions appearing at C would have taken place and the structure would appear as in Fig. 457.

The alloys of which this diagram is typical are those of silver and copper, lead and antimony, etc.

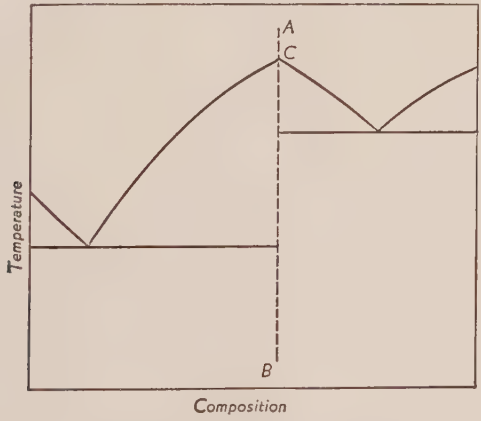

FIG. 459.

[12] EUTECTIC (from the Greek εὔτηκτος, easily melting), the alloy of a certain series possessing the lowest temperature of solidification. Their structures are made up of alternate plates or "lamellae" of the different constituents.

The equilibrium diagram of alloys whose component metals form a definite compound is shown in Fig. 459—the definite compound being formed at *C*. If this diagram is divided into two parts at the line *AB*, it is noticed that each of the parts resembles Fig. 455. The diagram, then, resolves itself into two systems, viz., alloys of one pure metal and the eutectic of that metal and the definite compound of the two metals, and alloys of the other pure metal and the eutectic of that metal and the definite compound.

The alloys of magnesium and tin form the definite compound of Mg_2Sn.

In addition to the phenomena observed in the transition from the liquid to the solid state, further changes occur in many alloys and upon which to a great extent their usefulness depends. These changes, usually accompanied by allotropic [13] modifications and consequently accompanied by changes in physical properties, are also marked by evolutions of heat on cooling (absorptions of heat on heating) and are attended by variations in structure often readily discernible by means of a metallographic examination. It is due to a knowledge of the laws governing these modifications that it is possible to regulate and control the physical properties of an alloy by means of heat treatment.

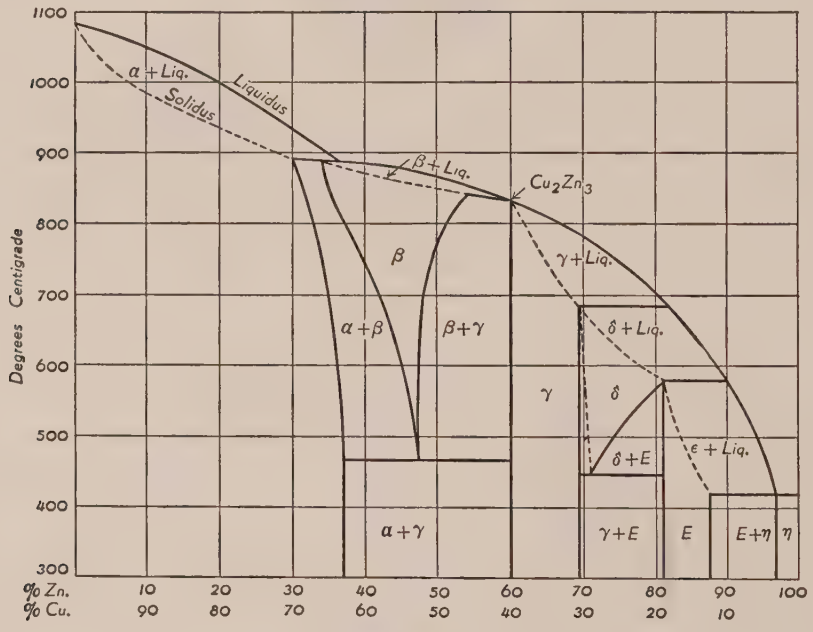

Fig. 460.

[13] Allotropy. A change in the properties of an element without change of state. Probably due to a change in the number or in the arrangement of the atoms in the molecule. Best defined by the example of the three allotropic forms of carbon, viz., diamond, graphite, coke (amorphous).

COPPER-ZINC ALLOYS

The application of the principles of metallography in connection with only one of the commercial non-ferrous alloys will be discussed and in a general way due to the somewhat greater importance of iron and steel in the industrial world and because the metallography of iron and steel embodies in a greater degree all the principles found in the metallography of the non-ferrous alloys.

Figure 460 [14] shows the equilibrium diagram of the brasses, an examination of which will show that the shape of the liquidus and solidus curves is of the type indicating the formation of a solid solution, except that in this case there are several solid solutions occurring instead of one. Below the solidus the existence of several different constituents can be noted which are formed after the metal has solidified and known as alpha, beta and gamma, etc. There are, however, practically no commercial alloys containing more than 60% zinc and so it is only necessary that attention be given to the alloys containing less than that amount.

FIG. 461. Photomicrograph of Brass Cold Rolled and Annealed. Magnified 100 diameters. Etched with ammonia and hydrogen peroxide.

Here there are three solid solutions, alpha, beta and gamma. The color of the alpha brasses varies from a pale yellow to a yellowish red, the color becoming redder as the copper content increases. These brasses have moderate tensile strength, high ductility and are suitable for cold rolling. Figure 461 is a photomicrograph of a section of alpha brass which has been cold rolled and annealed. Alloys containing the beta solution are somewhat harder and when cold are much less malleable and ductile. Beta brass has a greenish-red color and is darkened more quickly by the etching reagents than the alpha variety. Brasses containing the gamma solution being very brittel are without mechanical value and are only employed for castings of a purely ornamental character.

By regulating the amounts of copper and zinc and the temperature to which the alloy is heated and the rate of cooling from that temperature, the most advantageous properties of each of the constituents can be imparted to the metal. Mechanical working also improves the physical properties. Other metals are often added to copper-zinc alloys to make the alloy more suitable for the purpose for which it is to be used, e.g., iron, manganese, and aluminum are added in small quantities and increase the tenacity of the alloys considerably.

[14] After Hofman.

IRON-CARBON ALLOYS

The equilibrium diagram of the iron-carbon alloys is shown in Fig. 462.[15] By comparing the shape of the curves of the liquidus and solidus with those in Figs. 453 and 455, it may be seen that in the region embracing the steels, the alloys solidify as solid solutions; and in the region containing from about 2% to 5% carbon and in which fall the cast irons, a eutectic is formed.[16] Imme-

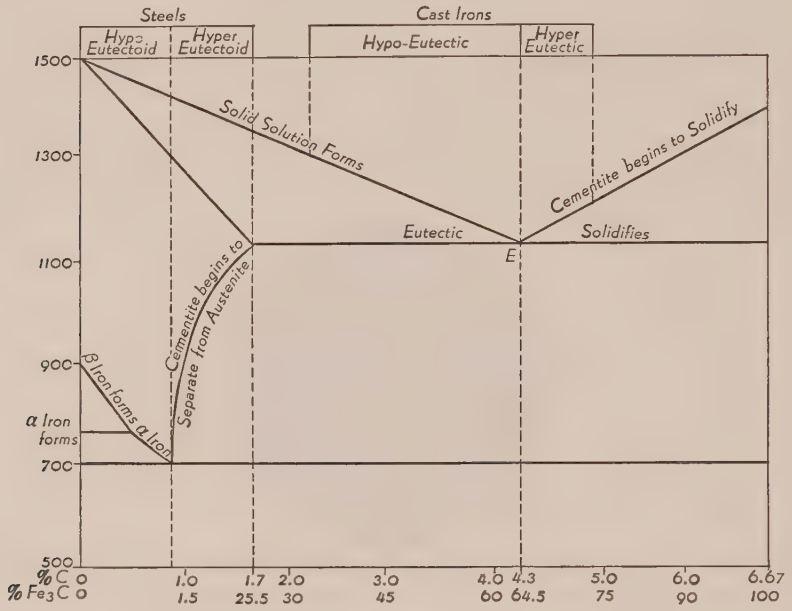

Fig. 462.

diately after solidification has taken place, the steels consist of a solid solution of carbon in gamma iron.[17] Gamma iron, then, will dissolve carbon until a total content of approximately 1.7% is reached at which point the solid solution becomes saturated and further increase in the amount of carbon results in the precipitation of the carbon in the form of the carbide of iron (Fe_3C) (called cementite) which forms a eutectic with the saturated austenite. At the point E the alloys solidify as 100% eutectic. With more than 4.3% carbon the constituent in excess of that necessary to form the eutectic is the carbide of iron.

[15] After Sauveur.

[16] The division between the steel series and the cast iron series is a purely arbitrary one, but the fact that there are very few commercial products containing between 1.7% and 2.5% carbon makes it a particularly convenient one.

[17] Many authorities define austenite as a solid solution of Fe_3C in gamma iron. Recent research, however, on crystal structure founded on X-ray examinations shows that independent molecules of Fe_3C do not exist in austenite. Z. Jeffries and R. S. Archer, Chem. and Met. Eng., **24**, 1057 (1921); **26**, 249 (1922).

In Fig. 463 is shown on a larger scale the transformations which take place in the steels after the metal has solidified. The shaded portions indicate the intensity of the critical points. It may be seen that pure iron has two critical points on cooling to atmospheric temperature, one occurring at about 900° C. and another at about 760° C. This indicates that iron exists in three allotropic forms—alpha, beta,[18] and gamma. The point marking the division between gamma and beta iron is known as the Ar_3 point [19] and the point marking the division between the beta and alpha iron is known as the Ar_2 point. As soon as any carbon is present, another point appears at about 690° C. (1274° F.) known as the Ar_1 point. When the carbon content reaches 0.4%, the two upper

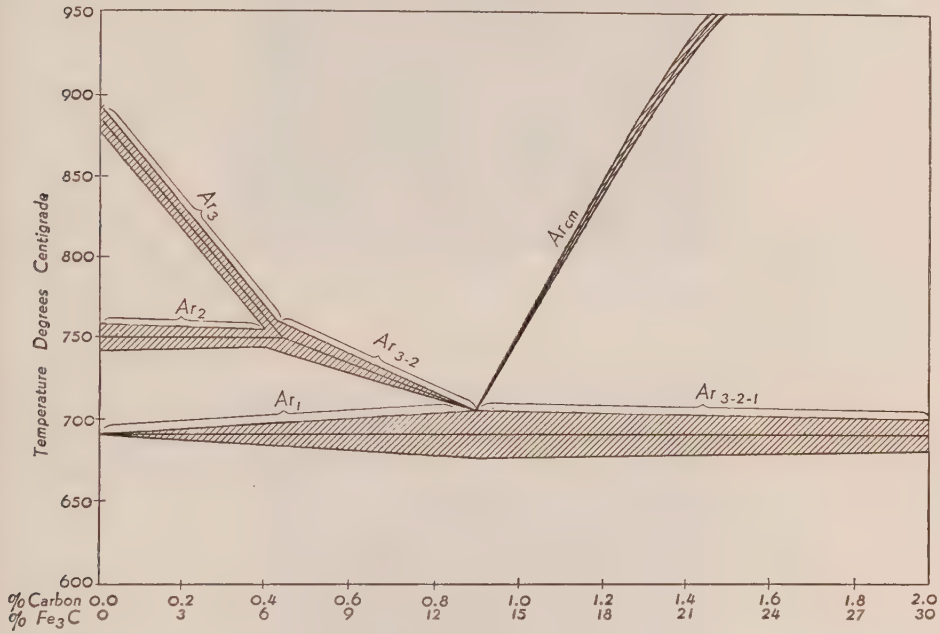

FIG. 463.

points merge forming a single point, $Ar_{3\text{-}2}$, which in turn merges at 0.85% carbon content with the Ar_1 point forming the $Ar_{3\text{-}2\text{-}1}$ point. From 0.85% carbon to about 2.0% carbon there are two points—the new point being known as the Ar_{cm} point.

It may be seen that the shape of these curves closely resembles that shown in the diagram illustrating the general type of curve representing the formation

[18] There is much controversy as to the presence of more than two allotropic forms. Some authorities contend that beta iron does not exist. Recently another allotropic modification has been noted as occurring at 1400° C. (2552° F.), denoting the presence of delta iron.

[19] The "r" in "Ar_3" etc. is the first letter of the French word "refroidissement." The points obtained on heating are "Ac_3" etc., the "c" being the first letter of the French word "chauffage." Due to hysteresis the transformation points occur at somewhat lower temperatures on cooling than on heating.

of a eutectic. On account of its analogy to this diagram as evidenced by the mechanism of the formation of the different constituents, and the thermal phenomena noted, the laminated structure formed on cooling 0.85% carbon steel has been named eutectoid.

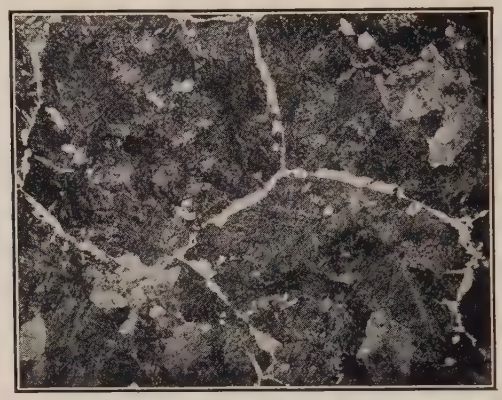

Fig. 464. Photomicrograph of 0.40% Carbon Steel (Cast). Magnified 100 diameters. Etched in a 4% alcoholic solution of nitric acid.

The four photomicrographs shown in Figs. 464, 465, 466, and 467 illustrate the structure of cast steel slowly cooled containing varying amounts of carbon.

The black constituent in the above photomicrograph is the eutectoid of iron and the carbide of iron called "pearlite" because of its resemblance in color with the naked eye to mother-of-pearl; the white constituent is made

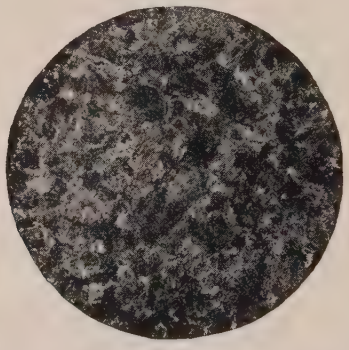

Fig. 465. Photomicrograph of 0.85% Carbon Steel (Cast). Magnified 100 diameters. Etched in a 4% alcoholic solution of nitric acid.

up of the crystals of iron (in excess of the eutectoid ratio) and is called "ferrite." Pearlite is relatively strong and hard, whereas ferrite is weak and soft.

Figure 465 shows the structure of slowly cooled steel which is made up of the single constituent pearlite, and Fig. 466 shows the same steel under a higher

magnification which brings out the characteristic laminations. In this photomicrograph the white constituent is the cementite and the dark constituent is the ferrite. (The ferrite is dark here because of its greater solubility in the etching reagent than the cementite and is consequently thrown in shadow.) Cementite is hard and strong, but very brittle.

FIG. 466. Photomicrograph of 0.85% Carbon Steel. Magnified 500 diameters. Etched with a 4% alcoholic solution of nitric acid.

The excess constituent is cementite—the needle-like forms in the grains of pearlite and the white substance at the grain boundaries.

FIG. 467. Photomicrograph of 1.25% Carbon Steel (Cast). Magnified 100 diameters. Etched in a 4% alcoholic solution of nitric acid.

The carbide of iron is an unstable compound and in the case of the cast irons at high temperatures is readily decomposed into graphite and iron. The result of this decomposition is that when the iron has cooled to atmospheric temperature, part of the carbon is present as Fe_3C, and part as free graphite. Certain impurities as well as the rate of cooling influence the breaking up of the carbide, e.g., silicon and slow cooling promote the formation of graphite, and manganese and fast cooling tend to keep the carbon in the combined

condition. Figure 468 shows the structure of cast iron and explains why this metal is weak, lacks ductility and cannot be forged or hammered. The black plates of graphite break up the continuity of the mass rendering it soft and weak.

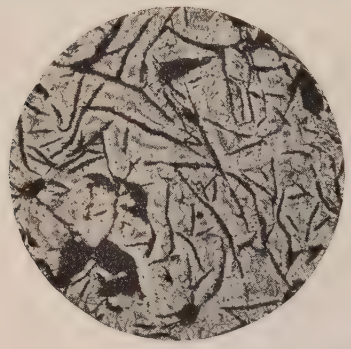

FIG. 468. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

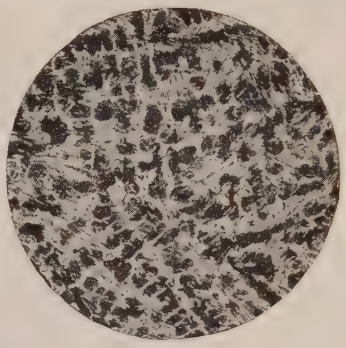

FIG. 469. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

If the percentage of silicon is low and the percentage of manganese is high, the carbon, in spite of a fast rate of cooling, will remain in the combined condition and the resultant product is "white" cast iron (so called from the appearance of its fracture as contrasted with that of "gray" cast iron). This metal although too brittle for commercial purposes is used for the production of the so-called malleable castings. Castings of this material are heated in large containers together with an oxidizing packing material to a

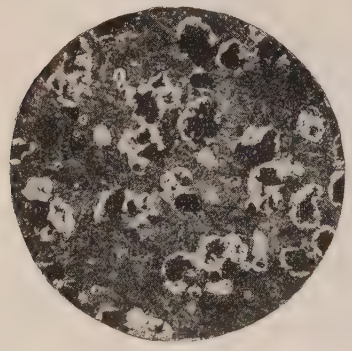

FIG. 470. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

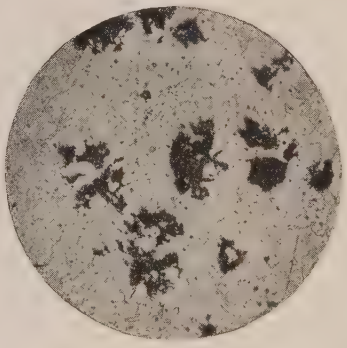

FIG. 471. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

high temperature for forty-eight hours or more, causing the carbide of iron to decompose into iron and graphite and a small amount of carbon to be removed from the surface. The graphite particles resulting from this decomposition due to their size and shape are less detrimental to the physical properties than

the plates present in gray cast iron. This may readily be seen in Figs. 469 and 471. The dark constituent in Fig. 469 is pearlite and the white is the carbide of iron. In Fig. 471 the black constituent is the graphite resulting from the breaking up of the Fe_3C and the white the ferrite.

Figure 470 shows the process only partly completed. The black areas are graphite, the lighter areas pearlite, and the white areas ferrite.

INFLUENCE OF MECHANICAL WORK

The purpose of hot work [20] such as forging, hammering, etc., is to shape the metal into useful articles and to decrease the size of the grains which greatly improves the physical properties, increasing the tensile strength and elastic limit. The diagram shown in Fig. 472 [21] depicts the influence of hot work on the structure of steel. While this is not strictly true for alloys other than steel, the same principles are involved.

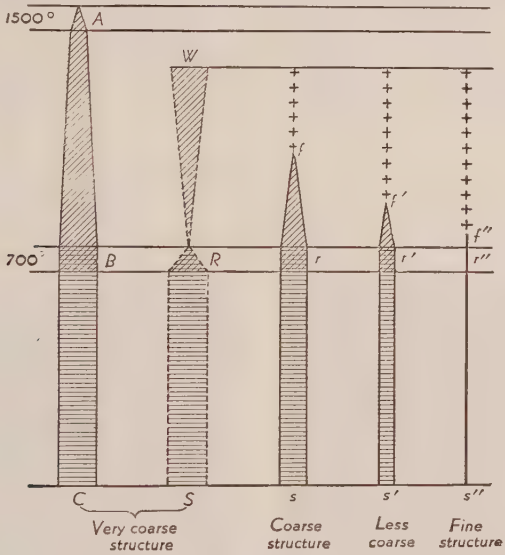

FIG. 472.

As the steel solidifies at A (or is reheated to W after the steel has cooled) the crystalline grains of the solid solution increase in size as the temperature falls to the critical range. In order to reduce this growth to a minimum, work should be stopped just above the critical range. If the work is stopped at f or f', a larger grain growth will result than if the work is stopped at f''. Work performed below the critical range when the metal is composed of an aggregate distorts the grains into elongated masses producing harmful internal strains.

In Figs. 473, 474, 475 are shown the structure resulting from hot working steels of different carbon content.

[20] The term "Hot Work" as used here denotes work performed above the critical range and "Cold Work" that performed below the critical range.

[21] After Sauveur.

Cold work is performed in wire drawing, rolling sheet steel, etc. It increases the elastic limit, tensile strength and hardness, and decreases the ductility as represented by the elongation and reduction of area.

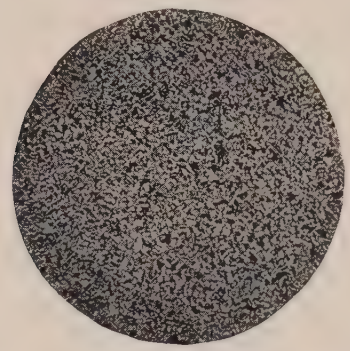

FIG. 473. Photomicrograph Showing Structure of Hot Worked .030% Carbon Steel. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid. Pearlite dark; ferrite white.

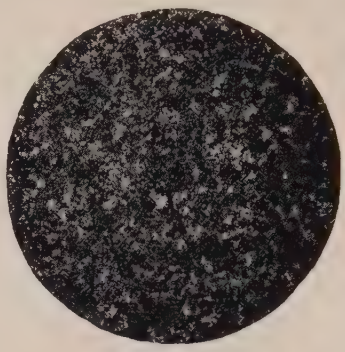

FIG. 474. Photomicrograph Showing Structure of Hot Worked Eutectoid Steel. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

The permanent deformation of metals results in the occurrence of certain characteristic changes in structure some of which are discernible under the microscope. The most important of these are: (1) Slip bands; [22] (2) Neumann lines; and so-called critical or exaggerated grain growth.[23]

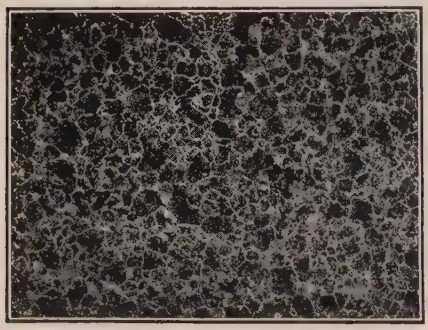

FIG. 475. Photomicrograph Showing the Structure of Hot Worked 1.25% Carbon Steel. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid. Pearlite dark; cementite white.

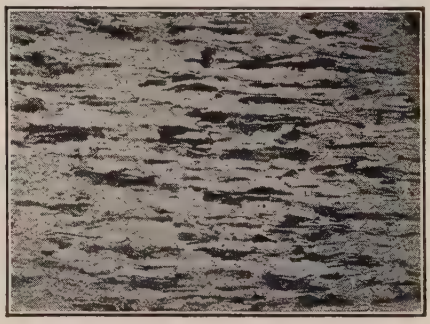

FIG. 476. Photomicrograph Showing the Structure Produced by Cold Work in a Steel Containing about 0.20% Carbon Magnified 100 Diameters. Etched with a 4% alcoholic solution of nitric acid. Pearlite dark; ferrite light.

Slip Bands.—Deformation under a slowly applied load is accomplished by a process of slip, i.e., the crystalline fragments of the grains slide on each other in much the same manner as a pile of books evenly stacked will slide on

[22] Z. Jeffries and R. S. Archer, Chem. and Met. Eng., Vol. 27, No. 18, p. 882.
[23] Sauveur, "Met. of Iron and Steel," p. 265.

one another if a force is exerted which disturbs them. The slip bands appear on polished and etched surfaces after the metal has been deformed as small hair lines (actually differences in level) for the most part running in one direction in the same grain, but in different directions in different grains. In some metals such as brass (see Fig. 461) annealing after cold work results in the

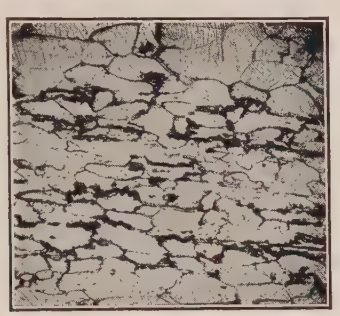

Fig. 477. Photomicrograph Showing Small Strip of Steel Slightly Bent after Polishing and Etching. Slip bands appear as black lines in those grains where the strain was greatest. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

formation of twins produced by part of the crystal having rotated through an angle of 180°.

Neumann Lines.—The appearance of these under the microscope is much the same as slip bands. They are, however, still present after repolishing

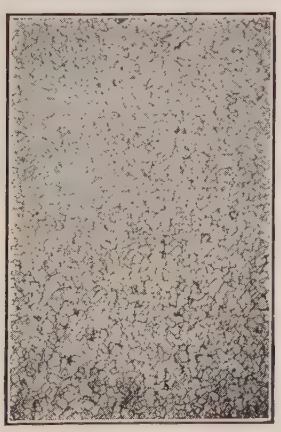

Fig. 478. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

Fig. 479. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

and etching whereas slip bands disappear. Their exact nature is not known but they are probably caused by a suddenly produced deformation, which may or may not have been accompanied by fracture.

Critical or Exaggerated Grain Growth.—This condition occurs in low carbon steel (.08% to 0.12%) strained by cold work corresponding to a 5 to 15% reduction and subsequently annealed at a temperature varying from 625° C. to 775° C. Steels composed of very large grains resulting from this treatment give poor results under both shock and fatigue stresses. Fig. 478 shows a low carbon steel in the normal condition and Fig. 479 after critical grain growth has taken place.

HEAT TREATMENT OF STEEL

Heat treatment as defined by Tiemann is "the change, or series of changes, in temperature, also the rate of cooling from one temperature to another brought about to secure certain desired conditions or properties in a metal or alloy." Heat treatment, in general, may be conveniently divided into three classes: (1) softening treatment; (2) hardening treatment; and (3) strengthening treatment.

There are three structural transformation changes that take place in steel as the metal cools through the critical range, each of which has definite physical properties and characteristic appearance under the microscope. Either one of these constituents or any combination of them may be retained in the metal when cold by cooling the steel through the critical range at different speeds, or by hardening followed by tempering. The names of the transformation constituents are martensite, troostite, and sorbite.

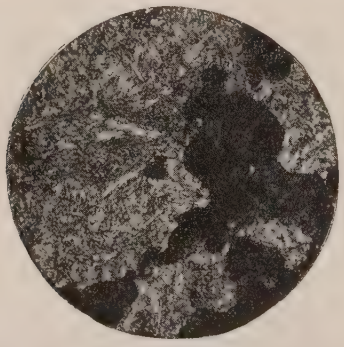

Fig. 480. Photomicrograph of 1.25% Carbon Steel Quenched in Water from Above the Critical Range. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid. Martensite light; troostite dark.

Fig. 481. Photomicrograph of 0.75% Carbon Steel Quenched in Oil from Above Its Critical Range and Reheated to 525° C. Magnified 100 diameters. Etched in a 4% alcoholic solution of nitric acid.

In order to produce maximum softness a very slow rate of cooling through the range is used which produces pearlite. To produce maximum hardness, the steel should be in the martensitic condition. This is obtained by cooling through the range at a fast rate, i.e., by quenching in water or oil. Such cooling should, theoretically, prevent any transformation from taking place, but in plain carbon steels partial transformation always occurs. If austenite is desired, certain other metals must be added which act as retarding agents on the transformation.

Steel containing 12% manganese or 25% nickel, for example, will remain austenitic even after slow cooling. Austenite is mineralogically softer than martensite, but is more resistant to abrasion. Under the microscope it has the general characteristics of a solid solution. Troostite is often present along with martensite in hardened steel and possesses similar physical properties, but in a lesser degree. Figure 480 shows the appearance of martensite and troostite.

Maximum strength combined with maximum ductility is obtained by producing the constituent sorbite. This can be done by cooling through the range at the proper speed, but more exactly by hardening followed by heating to a temperature between 400 and 600° C. according to the composition of the steel and the properties desired. Troostite may also be formed in such a manner if a lower reheating or "drawing" temperature is used. The appearance of sorbite when examined under the microscope is shown in Fig. 481.

CASE HARDENING

Case hardening, as the name implies, is the production of a hard case or shell on the surface of a soft steel in order to make it more resistant to wear without materially reducing its toughness and resistance to shock. Case hardening is made possible by the ability of iron when in the gamma condition to absorb carbon. The article to be so treated is packed in a suitable carbonaceous material and heated to a high temperature (about 950° C.) for a time depending upon the depth of case desired.

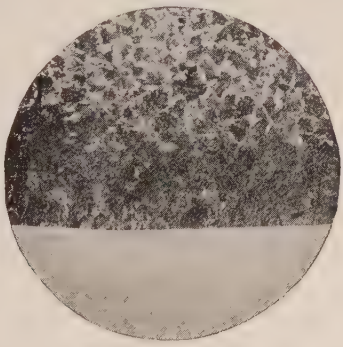

FIG. 482. Photomicrograph Showing the Edge of a Case-hardened Sample of Steel. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

The core and case may then be heat treated to further improve the physical properties. Case-hardened objects appear under the microscope as in Fig. 482.

INFLUENCE OF SOME ELEMENTS ON IRON AND STEEL

Manganese has a greater affinity for sulfur than iron and, therefore, if sulfur is present, manganese sulfide is formed. Under the microscope this appears in castings as small round areas, pale gray in color, and in forgings as elongated streaks of the same color. If there is any manganese remaining after the sulfide has formed, the carbide of manganese (Mn_3C) is produced, which forms a solid solution with the iron.

Sulfur, when present in small amounts (e.g., less than 0.08%), combines with the manganese as explained, but if in excess of this amount, the sulfide of iron (FeS) is produced which forms around the grains. Steel containing iron sulfide is weak and brittle at high temperatures. FeS appears a reddish brown under the microscope.

Phosphorus is present in solid solution as the phosphide of iron (Fe_3P). In cast irons, due to the large amount of carbon present, a eutectic of iron and the phosphide of iron is formed. Iron phosphide makes the steel brittle, especially when cold.

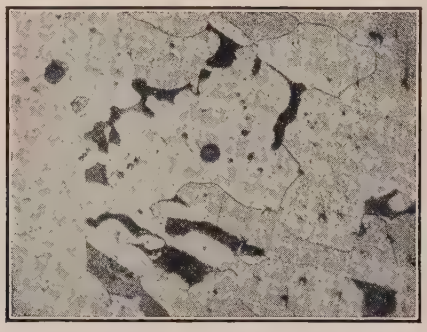

FIG. 483. Photomicrograph Showing Appearance of Manganese Sulfide (Small Round Areas Pale Gray in Color) in Low Carbon Cast Steel. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

Silicon is present as FeSi, which enters into solid solution with the iron. When in small amounts, silicon produces no marked influence on the physical properties.

Other elements such as nickel, chromium, vanadium, tungsten, and molybdenum are added to steel usually in amounts less than 5.0% which

FIG. 484. Photomicrograph Showing Appearance of Manganese Sulfide in Forged Low Carbon Steel (over 1.0% Sulfur). Pale gray colored areas drawn out in the direction of rolling. Magnified 100 diameters. Etched with a 4% alcoholic solution of nitric acid.

FIG. 485. Photomicrograph Showing Structure of Cast Manganese Steel (Manganese 12%) Austenitic. Small spots are undissolved carbides. Magnified 100 diameters. Etched with a 10% alcoholic solution of nitric acid.

FIG. 486. Photomicrograph Showing Structure of Cast High Speed Steel. Magnified 500 diameters. Etched with Yatsevitch's Reagent.

impart to the metal specially desired properties such as increase in hardness, without decrease in ductility, machine tools capable of cutting at a high speed, and for greater shock and fatigue-resisting properties.

METHODS FOR THE DETERMINATION OF SOLUBILITY [1]

A quantitative determination of a solubility consists essentially of two operations; the preparation of the saturated solution and its subsequent analysis. In those cases where these steps are performed separately the method may, in general, be designated as the analytical and in those where they are combined, as the synthetic. In both cases, however, the consideration of first importance is the assurance that final equilibrium between solvent and solute has been reached. Since this point is that at which no further change occurs in the relation between the amount of the compound in solution and that remaining undissolved, the only criterion of saturation is the evidence that the concentration of the solution has not changed during a longer or shorter interval of time, during which those conditions which would tend to promote such a change have been allowed to operate.

Of the conditions which promote most effectively the attainment of equilibrium between a solute and a solvent, the provision for the intimate contact of the two is most important. In other words, only by the thorough mixing which agitation or effective stirring provides can the point of saturation be reached with certainty. In the case of the reciprocal solubility of liquids, the point of equilibrium is usually attained within a much shorter period than in the case of solids dissolved in liquids. In the later case, the necessary disintegration of the solid, incident to its solution in the liquid, is a process which is restricted to the surface layers of the solid, and, therefore, unless a large area, such as a finely divided state provides, is available, and unless that portion of the solvent which has acted upon a given surface area is repeatedly replaced by fresh solvent, the process of solution will be greatly retarded. It is quite evident that, although a solution in contact with even very finely divided solid may promptly become saturated in the immediate vicinity of the solid without stirring, the distribution of the dissolved material to the remainder of the solvent would depend upon diffusion, and since the rate at which this proceeds would diminish as the concentration differences became equalized, the process would take place at a gradually diminishing rate. If the point of equilibrium is approached from supersaturation, the above remarks apply with equal effect, since only at the surface of the solid can the excess of salt leave the solution and, without other provision than diffusion for successively bringing the entire amount of the solution in contact with the solid, the deposition of the excess of dissolved material can occur only at a very slow rate. The importance of active and continuous agitation of the solid and solution, in effecting saturation, cannot, therefore, be too strongly emphasized. It may in fact be assumed that determinations of the solubility of solids, made without continuous agitation, are always open to the suspicion that the results do not represent the final equilibrium which such data are required to show.

[1] Reprinted from 2d Ed. of "Solubilities." Contributed by Atherton Seidell.

Since solubility is a function of temperature, the accurate control of the temperature in making a solubility determination is another one of the indispensible requisites of accuracy. In general, it may be stated therefore, that every procedure designed for preparing a saturated solution must include provision for the accurate control of the temperature and for active and continuous agitation or stirring of the solution. In the case of the solubility of gases, which will be considered in a separate section, provision for the control of the pressure must also be made.

It is obvious that since the solubilities of various compounds differ, and that of one compound is affected by the presence of another, the accurate determination of this constant for a particular molecular species presupposes that only this one substance is present in the pure solvent. That is, accuracy of results demand that only pure compounds be involved in a given determination, consequently, no effort should be spared to make it certain that the highest possible purity of both solute and solvent has been attained.

Apparatus for the Determination of the Solubility of Solids by the Analytical Method.—The types of apparatus which have been developed for the preparation of saturated solutions of solids in liquids differ principally in respect to whether designed for multiple or single determinations at a given temperature. Examples of the first type are illustrated by Figs. 487 and 488.

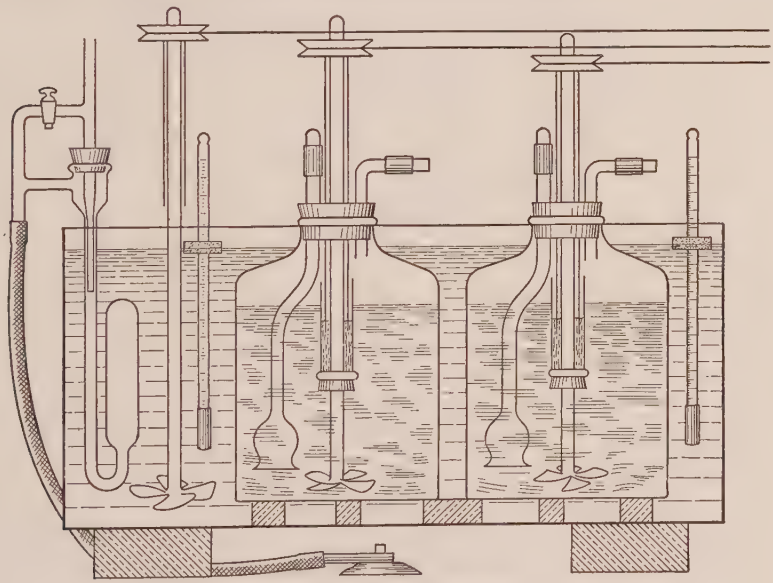

FIG. 487. Determination of Solubility of Solids.

It will be noted that in one case (Fig. 487) the bottles containing the solutions are stationary and the liquid in each and in the constant temperature bath is kept in motion by means of revolving stirrers. This form of apparatus was used by Moody and Leyson (1908) for the determination of the solubility of lime in water and is particularly adapted for relatively slightly soluble com-

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pounds for which rather large quantities of the saturated solution are needed for accurate analysis. There is also shown in the figure the provision for withdrawing the saturated solution through a filter within the inverted thistle tube. The stirrers in the bottles are fitted with mercury seals to prevent access of air containing carbon dioxide. Other features of the apparatus will be readily understood from the drawing.

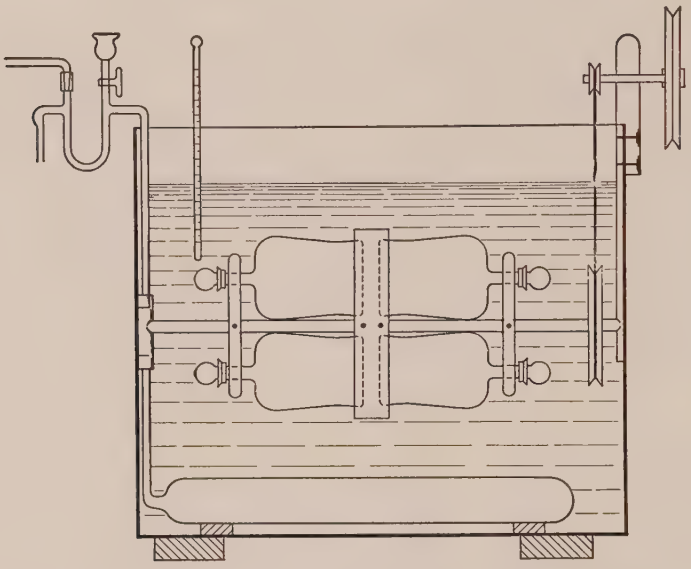

Fig. 488. Noyes Apparatus for Determining the Solubility of Solids.

A more common type of apparatus, designed for the simultaneous saturation of several solutions at the same temperature, is that illustrated by Fig. 488, in which the bottles containing the solutions are slowly rotated in the constant temperature bath. The form shown is that described by Noyes (1892). This type of apparatus has the advantage that the solid is, to a large extent, kept in suspension in the liquid and, therefore, offers the most favorable opportunity for continuous and uniform contact with the solution. Many examples of this form of apparatus, differing principally in size and in the direction of movement of the containers, are described in the literature.

Of the second type of apparatus, designed for a single determination at a given temperature, many varieties have been developed for particular conditions. Of these, the following examples have been selected as typical of this class and, it is hoped, will illustrate most of their desirable features. They are, in general, adaptations of earlier designs and it is not intended that the name given in connection with each is that of the investigator who deserves the credit for originating the type. The drawings will, for the most part, be readily understood without detailed explanations. The dimensions are not stated, since they can usually be varied to suit the needs of almost any problem.

In Fig. 489 is shown the apparatus used by the Earl of Berkeley (1904) for the very careful determinations of the solubility of inorganic salts in water. The features of particular interest in connection with it are, that the water bath itself is made to serve as the temperature regulating device, and the apparatus for withdrawing and simultaneously filtering the saturated solution is a combination of pipet and pycnometer. This was provided with ground glass caps for each end and the stem was accurately graduated. It was, of course, carefully standardized before use. The flexible iron plate shown was made of a disc from the receiver of a telephone. The apparatus was used for

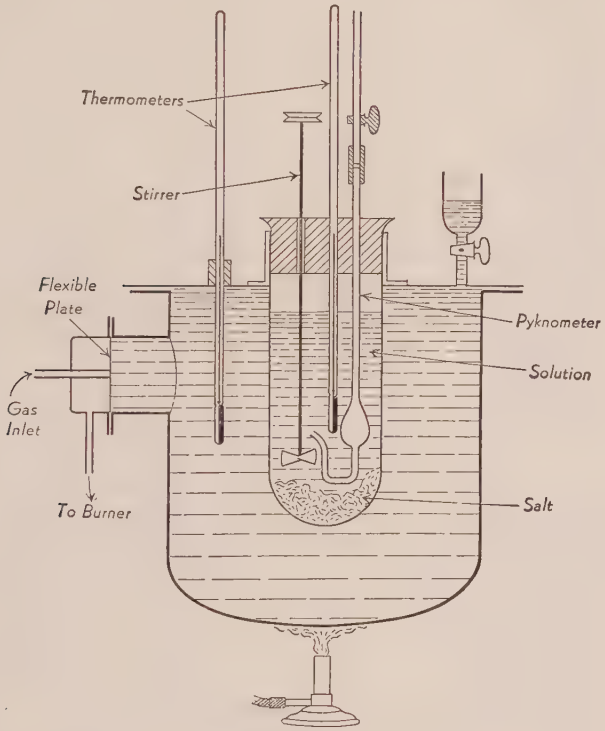

Fig. 489. Berkeley's Apparatus for Determining Solubility.

determinations at temperatures between 30° and 90° and the range of variations from the set temperature of the bath was, for 2–3 hour periods, within about 0.2°. For the inner vessel containing the salt, the range was about 0.05°. At each temperature two determinations of density and solubility were made; one on the solution obtained by stirring a supersaturated solution in contact with solid salt, and the other on the solution obtained by stirring an unsaturated solution in contact with an excess of salt.

In the case of determinations at the boiling point a special apparatus was required. Two forms, described by the Earl of Berkeley (1904), are shown in

Figs. 490 and 491. The first was used for the less soluble salts and consisted of an outer tube *A* containing water and an inner tube *B* containing salt and solution. By boiling the water vigorously and closing the side tube *C*, steam passing through the tube *D* stirred the solution thoroughly and the temperature rose to the boiling point of the saturated solution and remained constant when saturation was attained. The second form of apparatus (Fig. 491) was devised

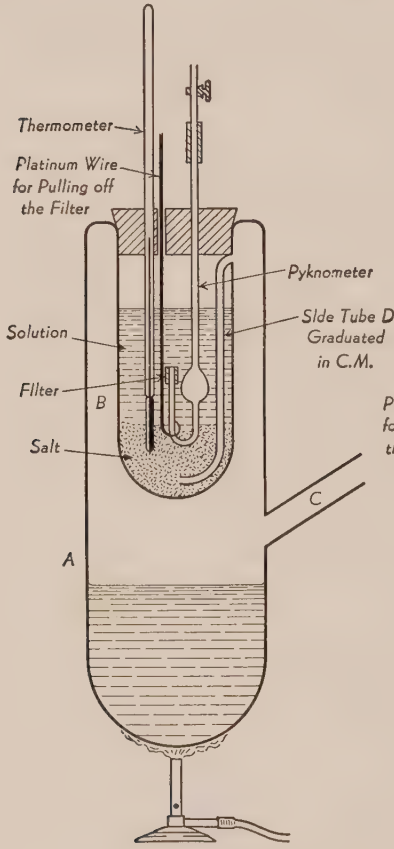

Fig. 490.

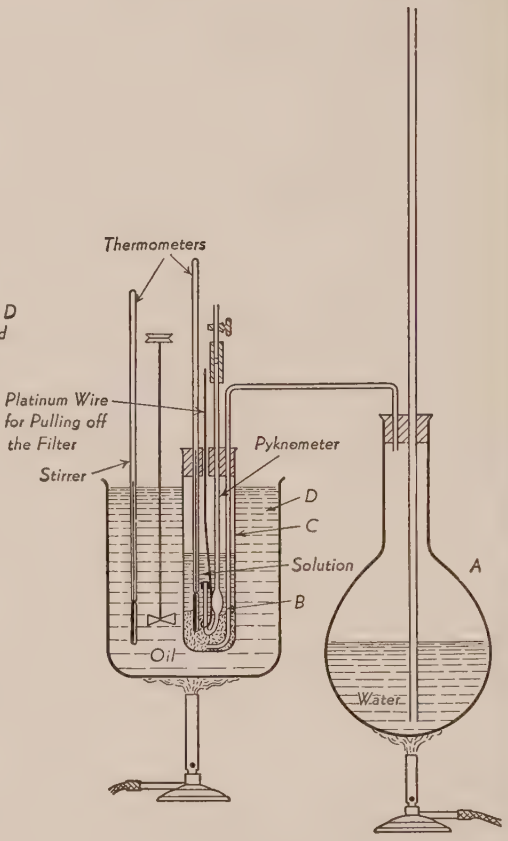

Fig. 491.

Berkeley's Apparatus for Determining Solubility.

for use with extremely soluble salts. In these cases it was found that the larger quantity of steam required for thorough stirring dissolved so much salt that it was necessary to have a very large excess present. In this apparatus the steam was generated in a boiler *A* and conducted through the tube *B* to the bottom of the large test tube *C* containing the excess of salt and solution. The test tube was immersed in the oil bath *D* which was vigorously stirred and maintained at a temperature close to that of the boiling point of the saturated

solution. When the temperature of the oil bath was below the boiling point, salt dissolved; when above, salt was thrown out of solution. Considerable difficulty was experienced in filling the pycnometer with the saturated solution without introducing errors due to steam bubbles caused by the suction which was applied.

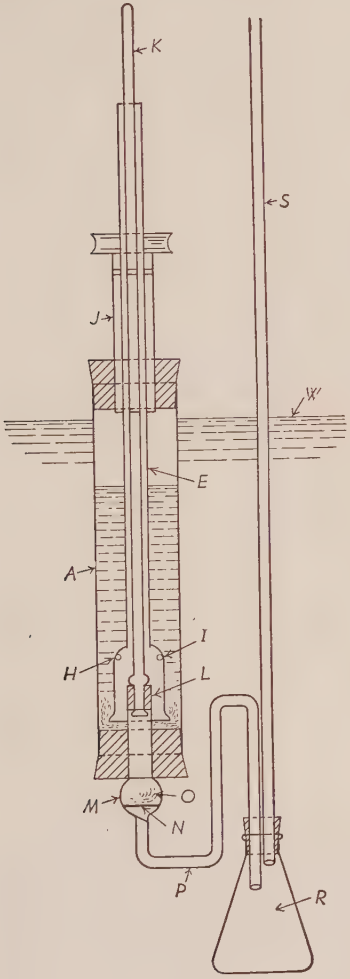

FIG. 492.

Victor Meyer Type of Apparatus for Solubility Determination.

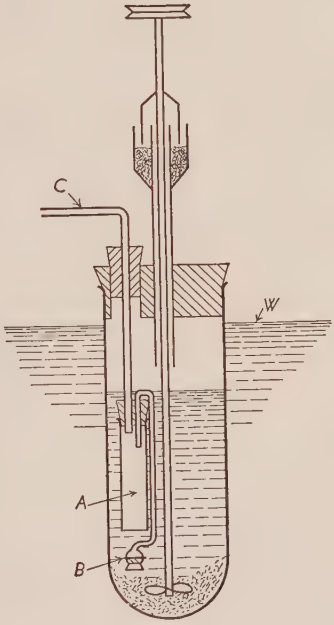

FIG. 493.

Walton and Judd Apparatus for Solubilities.

A comparatively simple form of the type of apparatus used by Victor Meyer in 1875 and modified by Reicher and van Deventer (1890) and by Goldschmidt (1895), is described by Hicks (1915) and shown in the accom-

panying Fig. 492. A glass cylinder *A* is closed at each end with large one-hole rubber stoppers. The mixture of salt and solution is contained in this cylinder and is stirred by the rotation of the tube *E* which is provided with an enlargement at its lower end in which there are two small holes at *H* and *I*. The stirrer rotates in the bearing formed by the hollow wooden cylinder *J*. The glass rod *K* carries a rubber stopper *L* which closes the filtering tube *M*, in which a platinum cone *N* supports an asbestos filter *O*. The siphon *P* connects the filtering tube with the flask *R* which is provided with an outlet through the small tube *S*. The apparatus is immersed in a constant temperature water bath *W*, to about the level shown. After stirring the mixture of salt and

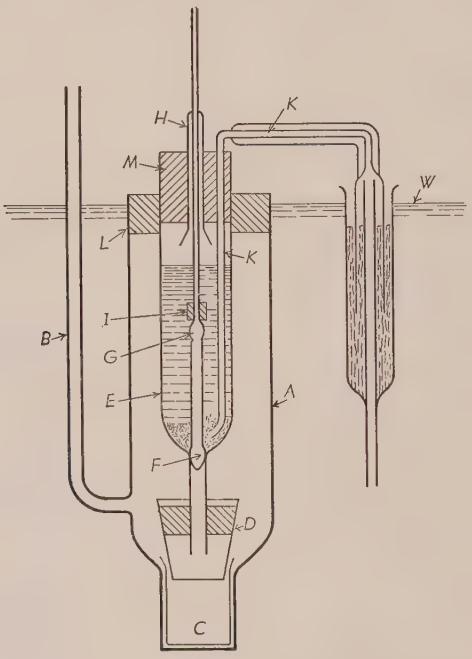

Fig. 494. Donnan and White Apparatus for Determining Solubilities.

solution a sufficient length of time for attainment of saturation, the undissolved salt is allowed to settle and the rubber stopper is withdrawn from the filter tube by means of the glass rod *K*. Suction is applied through the tube *S* to hasten the filtering and the clear solution collected, at the temperature of the bath, in the previously weighed flask *R*.

A similar apparatus was used by Walton and Judd (1911), for determination of the solubility of lead nitrate in pyridine. This is shown in Fig. 493 and consists of a glass test tube fitted with a stirrer which turns in a mercury seal, thus preventing loss of solvent by evaporation or the admission of moisture from the air. To take a sample of the saturated solution, the weighing tube *A* was introduced into the larger tube through a hole in the stopper. After reaching

the temperature of the bath the stirrer was stopped, the end of the small tube *B*, which was covered with a piece of closely-woven muslin, was dipped below the surface of the solution and the liquid drawn into *A* by applying suction at *C*. The tube *A* was then removed, weighed and the contents analyzed.

An apparatus which was used by Donnan and White (1911), for the determination of equilibrium in the system palmitic acid and sodium palmitate is shown in Fig. 494. The stirring in this case was accomplished by means of a current of dry air, free of carbon dioxide. The apparatus consists of two parts, namely, an inner chamber *E*, where equilibrium was attained, and an outer case *A*, designed for isothermal filtration. The whole was immersed in a thermostat to the level *W*. A side tube *B* permitted connection with a filter pump. *C* is a weighing bottle to receive the filtered saturated solution and *D* a Gooch crucible provided with a paper filter. The cork, closing *A*, was covered with a plastic layer to render it airtight. The tube at the lower end of *E* was closed with a ground glass plug *F*, the stem of which was enlarged to a small bulb at *G* and then drawn out to pass easily through *H*, leaving an air free outlet around it. The small cork *I* was used to support the stopper when lifted to allow the contents of *E* to flow down for filtration. The dry air by which the mixture was stirred was drawn through *K* by applying suction at *H*. The preheating of this air was accomplished by drawing it through a thin spiral immersed in the thermostat. The connection between the equilibrium apparatus and preheater was made through a mercury seal, which permitted lifting the apparatus easily without damage to the fragile preheater permanently mounted in the bath. This apparatus provided for the recovery, separately, of the saturated solution and undissolved solid. These authors also describe an improved electrically heated and controlled constant temperature bath.

Determinations at lower temperatures that can be constantly maintained with the aid of a water bath require special forms of apparatus which permit of temperature control under more or less restricted conditions. An apparatus of this type, which was used by Cohen and Inouye (1910), for determination of the solubility of phosphorus in carbon disulfide, is shown in Fig. 495, and is intended for the range of temperature between $-10°$ and $+10°$. The saturating vessel *D* consists of a glass cylinder to the upper end of which is cemented a steel collar *E*, containing a deep channel. A mixture of litharge and glycerol was used as the cementing material for this purpose. The inverted steel cover *F* fits into the channel of this collar and the seal of the joint is effected, in the usual way, by means of a layer of mercury. The cover *F* is provided with a brass tube *K*, to which the pulley *M* is attached, and is also pierced by the tightly cemented-in glass tube *I*. The glass rod *G*, containing on its lower end the three stirring wings *H H H*, is cemented into the brass tube *K*. The saturating vessel is, for stability, tightly fastened in a hole in a block of lead, *S*, contained in the Dewar cylinder *A*. An atmosphere of CO_2 in the saturating vessel is provided by introducing CO_2 under pressure through *I* and allowing the excess to escape through the mercury seal in *E*. After charging the apparatus, *I* is closed with a rubber tube and plug and the stirrers *H H H* set in motion. A Witt stirrer, *O*, keeps the contents of the bath in rapid circulation. Water is used in the bath for temperatures about 0°, and alcohol for those below 0°. The regulation of the temperature is accomplished by addition

of ice or solid CO_2 as found necessary and, therefore, requires very close attention on the part of the experimenter.

A novel and simple form of apparatus, which was used by Bahr (1911), for the determination of the solubility of thallium hydroxide at temperatures up to 40° is shown in Fig. 496. As will be seen, this consists of a gas washing flask to the arms of which a *Y* tube provided with two stop-cocks is sealed. The inside walls of the apparatus were coated with hard paraffin and the

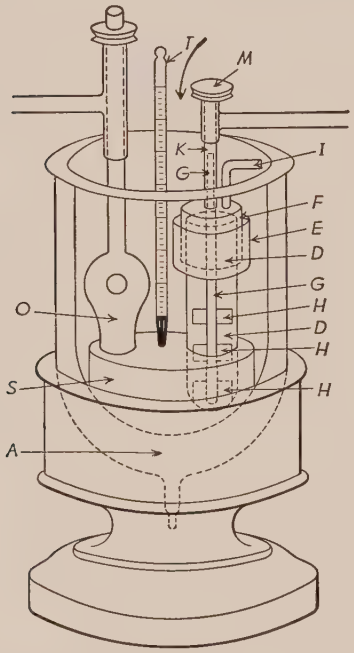

Fig. 495. Cohen and Inouye Apparatus for Solubilities.

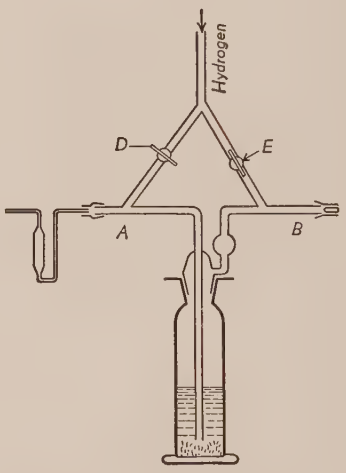

Fig. 496. Bahr's Apparatus for Determining Solubilities.

required amounts of thallium hydroxide and water introduced. It was then immersed in a water bath and the contents stirred by means of a current of hydrogen, which entered as shown and with *A* and *E* closed, passed through *D* and out at *B*. When it was desired to remove a sample of the solution for analysis, *B* and *D* were closed and the liquid forced through *A* into the pycnometer by means of gas pressure entering through *E*. For temperatures above 40°, the form of apparatus shown in Fig. 497 was used. In this case *K* represents a copper cylinder with double walls, of which the inner compartment *G*, contains concentrated salt solution which is stirred by a stream of air (not shown), and the outer compartment contains a layer of heating liquid *H*. The glass tube *L* contains the mixture of thallium hydroxide and water which is stirred by means of a current of hydrogen (not shown). When saturation is attained the tube *A*, of small bore and thick walls and provided with a small

asbestos filter, is introduced and the saturated solution forced over into the receptacle *B* by pressure of hydrogen which enters at *C*. The heating liquid in *B* is the same as used in *H*. The following heating liquids with the boiling points shown were used: Allyl chloride, 46°; Ethylene chloride, 55°; Chloroform, 61°; Methyl alcohol, 66°; Benzene, 80°; Benzene-Toluene mixture, 91°; Water, 100°.

A somewhat more elaborate apparatus, in which the constant temperature is maintained by means of the vapor of a boiling liquid, is shown in Fig. 498. This apparatus was developed by Tyrer (1910) for the very accurate determination of the solubilities of anthraquinone, anthracene and phenanthra-quinone in single and mixed organic solvents. The solvent with excess of the solute was placed in *A* and kept in constant agitation by means of the vertically acting stirrer shown. The tube *A* is surrounded by a bath of vapor which circulates through the cylinder *B*, condenses in *C*, and returns to the boiling flask *M*. When the solution is saturated it is allowed to settle, and the clear solution run out (by raising the tube *D*) into a small graduated flask *E*, which is maintained at the same temperature as the solution *A*. The temperature of the vapor bath is varied by changing the pressure under which the liquid in the flask *M* is boiling. For this purpose, the manostat *P* is provided. The temperature can, with care, be maintained constant to 0.01°. For this purpose the apparatus must be airtight, the liquid in the boiling flask must not bump (which is entirely prevented by placing a layer of mercury in the flask) and a pure boiling liquid must be used.

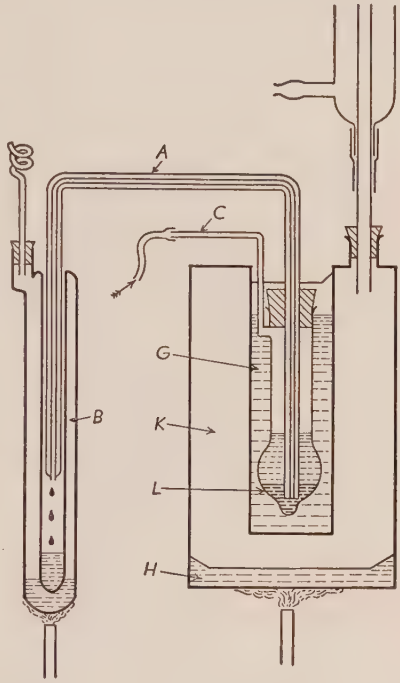

FIG. 497.

Although illustrations of special forms of apparatus designed for securing equilibrium in solubility determinations could be extended far beyond the number given, it is believed that the principal features have been made clear and it will no doubt be possible to adapt the devices here shown to many other cases for which accurate determinations of solubility may be desired.

Separation of Saturated Solution from Undissolved Solid.—The next point, after the establishment of equilibrium between the solvent and solution, is the matter of successfully separating the saturated solution from the undissolved solid, preparatory to its analysis. There are, undoubtedly, many cases where this is a very serious problem. This is especially so for extremely soluble compounds, which yield viscous solutions as well as for those which do not readily settle out of the solution or cannot be removed by ordinary filtration. It is,

of course, necessary to maintain the mixture at the temperature at which saturation was obtained until the complete separation of the solution and solid has been effected. The operation should, therefore, as a general thing, be conducted in the same bath used for preparing the saturated solution. Several forms of apparatus designed for this purpose are shown in the diagrams given in the preceding pages. For solutions which can be readily separated from the undissolved solid, a graduated pipet to which a stem with a plug of filtering material can be attached and which is adapted to being easily weighed, is the most convenient.

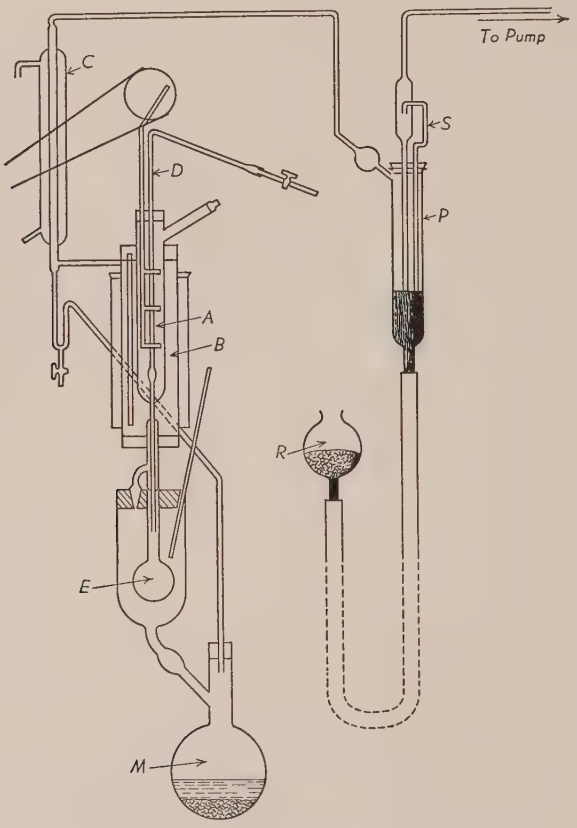

Fig. 498. Tyrer's Apparatus for Solubilities.

Analysis of the Saturated Solution.—The weight of a known volume of the perfectly clear solution, that is, its specific gravity, should always be determined. This weighed quantity of solution, or a known dilution of it, furnishes a very convenient sample for the determination of the amount of dissolved compound.

In regard to the analysis, the procedure must be selected entirely on the basis of the number and character of the constituents present. In cases of the

solubility of single non-volatile compounds, in solvents which can be more or less easily removed by volatilization, the plan in most general use is the vaporation of a known amount of the solution to dryness and weighing the residue. Special forms of apparatus to be used for this purpose have been proposed from time to time. These are, usually, vessels with tubular openings, arranged so that a current of dry air can be drawn over the surface of the heated sample.

In the case of solubility determinations in which the saturated solution contains more than one dissolved compound, the application of the usual gravimetric or volumetric procedures will, of course, be necessary.

In certain cases, where the direct determination of the amount of the dissolved compound present in the solution would be very difficult or impossible, an indirect method can sometimes be used. For this purpose, a carefully weighed amount of the compound must be used, and, after the period of saturation, the undissolved residue is filtered off under conditions which reduce losses to a minimum and, after drying to its original condition, it is weighed, and the amount which has been dissolved found by subtracting the weight of the undissolved residue from the quantity originally present.

Identification of the Solid Phase.—The solubility of a compound, which is capable of existing in several forms, depends upon the particular form in which it is present in contact with the saturated solution. The question of the composition of the solid phase is, therefore, of considerable importance for the accurate determination of solubility. Although the identification of the solid phase presents little difficulty in the majority of cases, it sometimes happens that it can be made only by a more or less indirect method. The principal reason for this is that adhering solution can usually not be completely removed from the solid phase and the analysis, consequently, does not give direct information of the required accuracy.

A method which has been used considerably for identifying the solid phase is that known as the *residue method* of Schreinemakers (1893). It is based on the principal that if an analysis is made of both the saturated solution and of a mixture of the saturated solution and the solid phase of unknown composition, the two points so obtained, when plotted on a coördinate system, lie on a line connecting the point representing the composition of the solid phase and the solubility curve of the system. Similar analyses of another saturated solution of the system and of its mixture with the solid phase, locate another such line. Since all lines so determined when extended, pass through the point representing the composition of the solid phase, their intersection locates this point definitely.

Although the original description of this method by Schreinemakers was illustrated by an example drawn on the rectangular system of coordinates, it has been used much more extensively, in a practical way, in connection with the later developed equilateral triangular diagram. In this case, each apex of the triangle represents one of the three components of the system, each point on a leg, a mixture of two, and each point within the triangle a mixture of all three components. When a number of saturated solutions are analyzed, the results correspond to points on the solubility curve of the system. If now some of the solid phase with adhering solution is removed from each mixture and analyzed, it is evident that the results thus obtained, being for samples made up of both the saturated solution and the solid phase, give points which lie on

lines connecting the two. The points on the curve for the pure saturated solutions being known, it is necessary only to connect them with the points for the corresponding mixtures of solid phase and saturated solution, and to prolong the lines to their common intersection. This will necessarily be at the point representing the composition of the pure solid phase.

In applying the residue method of Schreinemakers, if the intersecting lines which fix the point corresponding to the solid phase meet at a very narrow angle, definite information as to its composition may not be secured. For cases such as these, a procedure to which the name *"tell-tale"* method was given by Kenrick (1908) and which is described in detail by Cameron and Bell (1910), has been developed. This method consists in adding to the mixture a small amount of an entirely different compound which remains wholly in the solution. After equilibrium has been reached, a portion of the saturated solution and of the solid phase with adhering solution are analyzed, and the quantity of the added "tell-tale" compound in each determined. From the result, showing the concentration of the added compound in the saturated solution, and the amount of it found in the mixture of solid and solution, the quantity of solution in contact with the solid can be calculated. Since the composition of the solution is also known, the difference between the composition of the solid plus solution and of the amount of solution known to be present, is the composition of the pure solid.

Transition Temperatures can frequently be accurately determined by relatively simple means, and since such data are useful in establishing fixed points on solubility curves they are valuable adjuncts to directly determined solubility data.

Synthetic Method.—The procedures which have, so far, been mentioned are all classed as analytical methods of solubility determination. In contradistinction to these is the equally useful reverse process, by which the solvent and solute are brought together in previously measured quantities and the temperature ascertained at which the solution is saturated. To this procedure the designation synthetic method of solubility determination has been applied. One of the earliest investigators to use this method extensively was Alexejeff (1886) and it is, therefore, frequently referred to as the Alexejeff synthetic method of solubility determination.

The synthetic method can, of course, be used both for the solubility of solids in liquids and for liquids in liquids, but it is in the latter case that it is of greatest service. Its points of superiority, particularly in the case of the reciprocal solubility of liquids, are that the upper limits of the determinations can be extended far beyond the boiling point temperature and are, in fact, limited only by the resistance of the glass to pressure or to the action of the liquid. Only small quantities of the solute and solvent are required for a determination. It is applicable to compounds for which quantitative methods of analysis are not available or are of a tedious character. The mixtures, being contained in sealed tubes, are not subject to the action of constituents of the air, nor are losses, due to volatilization, to be feared. Although, in the case of solids, difficulties incident to the supersaturation, resulting from failure of the crystals to separate on cooling, are encountered, with liquids the point of saturation is made instantly and strikingly evident by the beginning of opalescence or clouding which occurs, and errors due to supersaturation are rarely

encountered. A sure criterion that supersaturation does not occur rests on the observation of the temperature at which the cloudy solution again clears. If this temperature coincides with the temperature of the beginning of opalescence, it is certain that supersaturation has not occurred. The observation of the temperature of saturation can be repeated as often as desired, and the accuracy of the determination is ordinarily limited only by the care taken in making it.

The limitations of the method, aside from the supersaturation which may occur in the case of solids, are principally those resulting from the low temperature coefficients of solubility possessed by certain compounds, and which usually occur in the vicinity of maxima or minima of solubility curves. Although a "critical clouding" occurs in the vicinity of the so-called critical solution point, this possesses a characteristic appearance which is easily distinguishable from the clouding observed at the saturation point, and errors of observation due to it are not to be apprehended. In fact, it has been pointed out that supersaturation disappears at the critical point, and the synthetic method is ordinarily very accurate in the vicinity of the critical solution temperature.

Since, by the synthetic method the results are necessarily obtained under different pressures, this question has been given consideration from the theoretical and the practical side. Although it is possible that extremely high pressures would exert an influence, the conclusion appears justified that under ordinary conditions, in which pressures of 10 atmospheres are not exceeded, no notable effect would be produced. The solubility curves obtained by this method do not show any abnormalities due to this cause.

In the case of the determination of the solubility of solids by the synthetic method, the operation consists in preparing a mixture of a carefully determined amount of the solvent and of the solid, and subjecting it to gradually increasing temperature and to constant agitation, while a continual observation of the changes taking place in the solid is made. When all but a few small crystals have dissolved, the change in temperature is regulated much more carefully and note is taken of the point at which the edges of these final crystals begin to change from sharp to rounded, or vice versa, or where the sizes of the particles visibly increase or diminish. Care must, of course, be taken not to allow the last portions of the solid to dissolve; otherwise, on cooling, considerable supersaturation may occur before the solid begins to separate from solution. The method is, naturally, most serviceable where the change in solubility with temperature is considerable, and where convenient methods for the direct analysis of the solution are not available.

The procedure of a determination in the case of the reciprocal solubility of liquids consists in introducing by means of capillary funnels weighed amounts of the two liquids into small glass tubes and sealing the ends. The amount of air space in the tubes should be kept low. Many convenient devices for weighing and introducing the liquids have been described. In the case of very volatile liquids it may be necessary to introduce them in thin walled bulbs, which can be broken after the tube containing the mixture has been sealed. The tube is then placed in a large beaker of water, or higher boiling liquid if necessary, and heat applied until the contents of the tube, on being shaken, become homogeneous. The temperature is then allowed to fall very slowly and an observation made, while the tube is constantly agitated, of the tempera-

ture of first appearance of opalescence. This observation can be repeated as many times as desired and the temperatures of appearance and disappearance of the clouding, which usually differ by only a few tenths of a degree, can be ascertained with certainty.

Since, by the synthetic method the data are for irregular intervals of temperature, in order to obtain results for a particular temperature it is necessary to plot the several determinations on coördinate paper and from the solubility curve so obtained, read the value for the temperature in question.

Freezing-point Method.—A modification of the synthetic method, which is applicable particularly to solutions which contain relatively large amounts of the dissolved compound, is that which consists in a determination of the freezing-point of the mixture. This point is, in fact, the temperature at which the separating solid compound is in equilibrium with the solution.

The difference between the freezing-point determination and the observation of the point of growth or diminution of a crystal in a liquid is that, in the former, the establishment of equilibrium is recognized exclusively by the change of the thermometer. The solution is cooled gradually, during which the thermometer sinks slowly to a point below the freezing temperature. As soon as the first crystal appears, either spontaneously or by intentional introduction (seeding), the thermometer rises suddenly to the freezing-point and remains stationary for some time.

This method can, of course, be used in a large number of cases for the determination of solubility. Those portions of the solubility curves of salts in water for which ice is the solid phase, are practically always determined in this way and it may be said, in general, that for determinations made at low temperatures, the freezing-point method is to be selected whenever possible.

For the practical execution of the method the very well known apparatus of Beckmann is most convenient and satisfactory. The determinations must, of course, be made with all the refinements which have been developed for accurate freezing-point measurements.

The method has been used extensively for the discovery of addition compounds. Its use for this purpose is based upon the principle that if to a pure compound, A, a second, B, is added, the freezing-point of A is lowered; similarly the freezing-point of B is lowered by A, and the two descending curves thus obtained intersect at the eutectic. If, however, a compound, A_xB_y is formed, this also acts as a pure substance and its freezing-point is lowered by either A or B. Hence the freezing-point lines do not meet at a single eutectic but exhibit in this case a maximum, the position of which indicates the composition of the compound.

Volume Change Method.—Still another method, which is a modification of the synthetic, is that designed to indicate the reciprocal solubility of liquids by a determination of the volume changes which occur when two relatively sparingly miscible liquids are shaken together in a closed vessel. The apparatus consists usually of a cylindrical receptacle which is provided with a constricted graduated section either at one end or near the middle. Such volumes of liquids are chosen that the meniscus separating them lies in the constricted graduated tube. The determination consists in superimposing measured volumes of each liquid and noting the position of the meniscus before and after a period of shaking at constant temperature. From the increase or

decrease of volume of the two layers, as estimated from the change in position of the meniscus, the reciprocal solubility of the two liquids is calculated. It is to be noted, however, that the solubility of liquids is in practically all cases reciprocal, and without an analysis of the two layers the true solubility can not usually be deduced.

Titration Method.—A special case of the reciprocal solubility of liquids is that representing equilibrium in ternary systems yielding two liquid layers. Such equilibria are usually determined by relatively simple titration procedures, but for the interpretation and description of the results, special terms have been developed and these require more or less detailed explanation.

When a third liquid is added to a mixture of two others which are miscible to only a slight extent, the added liquid, if soluble in each of the others, will distribute itself between the two and an equilibrium will be reached. If the two layers are then analyzed and the results plotted on coördinate paper, two points, corresponding to the two layers, will be obtained. If more of the third liquid is added, equilibrium will again be established after a short period of shaking and the analysis of the two layers, to which the designation *conjugate* layers has been given, will fix two more points when plotted on the coördinate paper. The process may be repeated until a considerable number of points have been obtained. When this has been done, it will always be found that these points are the locus of a smooth curve, to which the designation *binodal* curve has been given. If the pairs of points corresponding to the conjugate layers are connected, the lines so obtained are defined as *tie lines*. Since it is evident that with the continued addition of the third or *consolute* liquid, a point must finally be reached at which the resulting mixture will no longer separate into two conjugate layers, the tie lines successively determined as above described will become shorter and shorter until finally the last one is reduced to the point corresponding to the homogeneous mixture of the three components. To this is given the name *plait point.*

Although for the above example a ternary system made up of three liquids has been taken, there are a large number of salts and other solid compounds which, when dissolved in mixtures of liquids of certain concentrations, cause the latter to separate into conjugate liquid layers. These systems have aroused much interest from time to time and considerable data for them are given in the literature.

Since it is usually difficult and frequently impossible to analyze directly a homogeneous mixture of liquids, and thus determine the points on a binodal curve, a simple titration method for this purpose has come into general use. By means of this a homogeneous mixture of known amounts of two of the components is titrated with the third just to the point of initial separation of the second layer, which is usually very sharply indicated by the appearance of clouding or opalescence. The procedure may also be reversed and the consolute liquid added just to the point of clearing of the cloudy mixture of the other two. By this plan the synthetically derived composition of one of the two conjugate layers and thus of one point on the binodal curve is known. The determination of the tie line and therefore, the identification of the corresponding point on the curve for the conjugate liquid, requires an additional experiment for its location. Several procedures for this purpose have been developed. They usually depend upon the determination of one or more

constants of specially prepared pairs of conjugated liquids, such as their specific gravities or refractive indices. In the case of mixtures of which one member can be easily determined analytically, tie lines can be located by the quantitative determination of this member in pairs of conjugated liquids.

In general, the titration method for the determination of the solubility of liquids is applicable to many cases. The facts, that equilibrium is attained so promptly in liquids and that the evidence of the appearance of a second insoluble layer is usually so striking, make it of great value. Refinements have been introduced such as the addition of liquid or solid dyes to the mixture in order to facilitate the detection of the end point, and the development of particular forms of apparatus for measuring and weighing the liquids. The constituents of the mixtures are usually weighed but the volume relations and, therefore, the specific gravities can also be approximately estimated, by using graduated vessels for making the titrations, and measuring in them the volumes of the final mixtures.

As a usual thing the temperature coefficients are not very great in the case of liquid mixtures and the very accurate control of the temperature is not imperative. When such control is necessary, however, the use of a thermostat does not seriously complicate the determination.

Distribution Coefficients.—As mentioned above, when a third compound is added to a mixture of two liquids which are relatively immiscible, it will dissolve to a certain extent in each and the composition of the two layers represent conjugate points on the binodal curve for the system. The results are, however, of interest from another point of view, namely that of the distribution of the compound between the two solvents. This distribution coefficient is, in many cases, of considerable interest in connection with analytical methods based on shaking out procedures and also in connection with such problems as the molecular state of compounds in solution, their dissociation and other points of theoretical interest. Distribution coefficients have, therefore, been studied to a large extent and much data for them are available. In general, the determinations are made by relatively simple methods. The amount of the compound present in a definite amount of each layer, after equilibrium has been established by adequate agitation, is determined in any manner most convenient. If the total amount of solute is known, and that found in one layer, the amount in the other can, of course, be calculated by difference. The results are usually expressed on the volume basis, since it is the ratio of the amounts present in the same molecular state in equal volumes of the two layers which is a constant, independent of temperature and concentration.

It is evident that when the concentration at the saturation point is considered, the amount of the compound which enters each layer depends upon its solubility in the liquid, consequently the distribution coefficient is the relation of the solubilities of the dissolved substance in the two solvents. Variations from this, aside from changes in molecular state, etc., in one or the other solvent are due to such causes as the reciprocal solubility of the so-called immiscible solvents, which will, of course, be influenced by the presence of the dissolved compound, especially at the higher concentrations. Variations of the coefficient with temperature would result in cases where the solubilities of the compound in the two solvents do not change at the same rate with temperature.

Electrolytic Conductivity Method.—Of the physical properties which can be used for the determination of the concentration of a solution, such as

specific gravity, refractive index, etc., the electrolytic conductivity is of particular value in the case of those very sparingly soluble compounds which yield solutions too dilute to be analyzed by gravimetric or volumetric methods. By its use the progress of the saturation can be followed without separating the undissolved solid from the solution, or even removing the portion used for the determination. The special electrical equipment which is required, however, and the need for water of exceptional purity and of vessels of particular qualities, restrict its general use.

The method of calculating the concentration from the conductivity is based on the assumption that at the very great dilutions involved, complete dissociation occurs. Therefore, the limiting value to which the equivalent conductivity approaches at infinite dilution is, for practical purposes, attained, and $\Lambda = \Lambda_\infty = l_a + l_k$, where l_a and l_k are the ionic conductivities of the anions and kations. These values are known for all the principally occurring ions. The observed specific conductivity κ is, however, connected with the equivalent conductivity and the concentration η by the equation $\Lambda = \kappa/\eta$, in which η represents the concentration in gram-equivalents per cubic centimeter. Rearrangement and substitution give $\eta = \kappa/(l_a + l_k)$. From this equation the solubility of the substance under investigation is calculated by substituting the measured specific conductivity of the solution and the known values of the ionic conductivities.

The Solubility of Gases in Liquids.—When a gas and a liquid are intimately mixed by shaking, a definite amount of the gas will be dissolved by the liquid and, simultaneously, the vapor of the liquid will mix with the gas in the space above the liquid. The partial pressure of the liquid in the gas space is almost exactly the same as that of the pure liquid at the solution temperature, since the influence of the relatively slight amount of dissolved gas is insignificant in by far the most cases. The amount of gas which is dissolved depends both on the nature of the gas and of the liquid and is, furthermore, a function of the temperature, and pressure.

In regard to the influence of pressure, the absorption law of Henry holds for the most part, when the gas solubility is not too great. According to it, the amount of pure gas, which is taken up at constant temperature by a given amount of liquid is proportional to the pressure of the gas.

The temperature acts almost always in the sense that the solubility decreases as the temperature rises.

The solubilities of gases are usually expressed either in terms of the Bunsen "Absorption Coefficient" β,[1] or the Ostwald "Solubility Expression" l.[2]

[1] β = the **Bunsen Absorption Coefficient** which signifies the volume (v) of the gas (reduces to 0° and 760 mm.) taken up by unit volume (V) of the liquid when the pressure of the gas itself minus the vapor tension of the solvent is 760 mm.

$$\beta = \frac{v}{V(1+0.00367\,t)}.$$

[2] l = the **Ostwald Solubility Expression** which represents the ratio of the volume (v) of gas absorbed at any pressure and temperature, to the volume (V) of the absorbing liquid, i.e. $l = \frac{v}{V}$. This expression differs from the Bunsen Absorption Coefficient, β, in that the volume (v) of the dissolved gas is not reduced to 0° and 760 mm. The solubility l is therefore the volume of gas dissolved by unit volume ofthe solvent at the temperature of the experiment. The two expressions are related thus:

$$l = \beta(1+0.00367\,t), \qquad \beta = \frac{l}{(1+0.00367\,t)}.$$

The experimental methods for the determination of the solubility of gases vary according to the nature of the gas. For those which dissolve in relatively large amounts and can be analytically determined with accuracy, the saturated solution may be analyzed by ordinary quantitative methods. Thus, in the case of the solubility of sulfur dioxide in aqueous solutions of salts, the solutions were saturated by passing a stream of the gas through them at atmospheric pressure and, when equilibrium was attained, a measured portion of the solution was withdrawn, transferred to an excess of standardized iodine solution and the excess of the latter titrated with thiosulfate. A gravimetric procedure was used by Christoff (1905) for the determination of the solubility of carbon dioxide in aqueous salt solutions. In this case the solutions were weighed before and after the passage of the gas through them and the increase in weight, after applying necessary corrections, taken to represent the solubility at the temperature of the experiment and at atmospheric pressure. The absorption flasks were of special shape and the gas was previously passed through a series of U tubes, containing the same aqueous solution, in order to prevent loss of water from the experimental solution which, otherwise, would have occurred.

In the great majority of cases, however, gas solubility is determined by a method based upon the measurement of the volume of the gas absorbed. The apparatus consists essentially of an absorption flask for the liquid, connected by means of a tube of small bore to a graduated buret in which the gas is measured above mercury, the level of which can be altered by raising or lowering a container connected with the buret by means of a rubber tube. Many forms of this apparatus have been described and the disadvantages of the earlier forms have gradually been remedied. A relatively simple form of this apparatus, but one which embodies the essential features required for accuracy, is that described by McDaniel (1911) for the determination of the solubility of methane, ethane and ethylene in a large number of organic solvents at various temperatures.

This apparatus is shown in Fig. 499. *A* is an ordinary gas buret and *B* an absorption pipet of the form first used by Ostwald. "The buret and pipet are connected by means of the glass capillary *M* sealed directly onto each, so that the whole forms one solid piece of glass apparatus *without rubber or cement connections of any kind;* thus any possibility of leaks from these extremely troublesome sources is entirely avoided. The whole apparatus is clamped solidly to a rigid support so that it can be taken up in the hands and shaken for the purpose of bringing the gas into intimate contact with the liquid. The pipet and buret are each provided with a three-way stopcock, *C* and *D*. These can be turned in such a way as to allow the gas to sweep out the air from the connecting capillary. By the same means the two vessels may also be connected directly with each other as well as separately with the outside air or source of gas supply. The pipet and buret are each provided with a water jacket, *P* and *Q*. The temperature of each is regulated by means of the electrically heated coils *K* and *L*." These coils are of manganin wire and are connected in series. The rate of evolution of heat in the jackets was adjusted in the first place by varying the length of the manganin wire, until the temperature was the same in each jacket. Stirring was accomplished by blowing air through the tubes *I* and *J*. The differences in temperature between the pipet and buret were never greater than 0.1°.

In carrying out a determination by this method it is, of course, necessary that the solvent be completely free of dissolved air or other gas. This is perhaps the most important part of the determination and a special form of apparatus for the purpose is described by McDaniel (1911) and is shown in Fig. 500. "The liquid was boiled under diminished pressure in the flask *C* attached directly to the lower opening of the pipet by means of the rubber stopper as

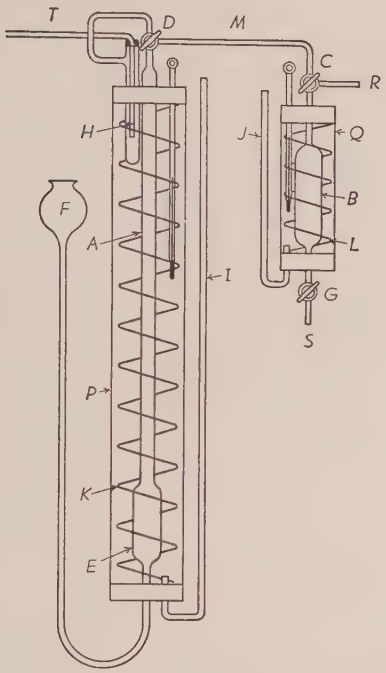

Fig. 499. McDaniel's apparatus for determining gas solubilities.

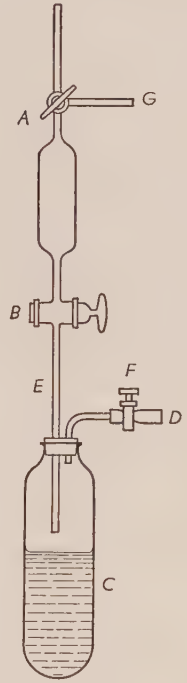

Fig. 500.

shown in the figure. Connection with the air pump is made at *D*. During the boiling the lower opening of the inlet tube *E* is above the surface of the liquid in *C*, the stopcock *B* being closed. When the air has been completely expelled, the screw pinchcock *F* is closed while the air pump is still in operation. The flask *C* is now raised until the lower end of *E* reaches nearly to the bottom of the flask. The air pump is now connected at *G* and the cock *A* opened so as to make connection with the pipet. *B* is now opened and the inflow of air through *D* regulated by gradually opening *F* in such a manner that the liquid is very slowly forced up into the pipet. In this manner the liquid never comes into contact with the air under full atmospheric pressure but only under greatly diminished pressure. The absorption of air under these conditions can only be inappreciable, especially since the liquid in the flask remains perfectly quiet, and only the lower portion is used."

Having filled the pipet *B*, Fig. 499, with the air-free solvent as just described, "*T* is connected with the source of gas supply and the cocks *C* and *D* are turned in such a way as to allow the gas to sweep out the air from the capillary, *M*. The buret is then filled in the usual manner by lowering the leveling tube *F*, the cock *D* having been turned so as to connect *T* with *E*. Care is taken to keep the entering gas under a slight pressure by keeping the mercury level in *F* slightly above that in *A*. This prevents air from entering through any leaks in the train connecting the gas generator with the buret." The gas must be completely saturated with the vapor of the solvent and this, with other than aqueous solvents, may require, in addition to drawing it through some of the solvent in *H*, that a thin layer be placed in the buret and time allowed for it to saturate the gas sample.

"After again allowing the current of gas to flow through the capillary *M* for a short time the buret and pipet are connected with each other by turning the three-way cocks *D* and *C* in the proper direction. The determination of the amount of absorption is then made as follows: A portion of the gas is passed into the pipet by raising *F* and opening *G*, the displaced liquid being caught in a graduated cylinder. The cock *C* is closed and the gas and liquid in the pipet brought into intimate contact with each other by shaking the whole apparatus. *C* is now opened to allow gas to enter from the buret to replace that absorbed. This process is repeated until, on opening *C*, there is no further decrease in the volume of gas in *A*. The volume absorbed is found by subtracting from the original volume of gas, the volume remaining in the buret plus the volume in the pipet. The volume of gas in the pipet is equal to the volume of liquid drawn off. The volume of liquid remaining is easily calculated from the known volume of the pipet. The absorption coefficient or 'solubility' is the ratio of the volume of gas absorbed, measured at the temperature of the experiment, to the volume of the saturated liquid. It may be reduced to the coefficient used by Bunsen by dividing by $(1+\alpha t)$."

In the case of the majority of investigators who have used this method, particularly for determinations at high or low temperatures, the absorption pipet has been kept at the temperature of the experiment and the gas measuring buret at room temperature, the two being connected by means of a flexible capillary which permits the absorption pipet to be independently shaken. This arrangement makes it necessary, in calculating the absorption coefficients, to apply the usual corrections for temperature and vapor pressure to the volume of gas in the buret. This is a complication which in some cases causes uncertainties in regard to the accuracy of the results as finally calculated.

An apparatus designed for determinations at very high pressures, using a Caillet compression tube, is described by Sander (1911–12). It was used for determination of the solubility of carbon dioxide in water, alcohols, and other organic solvents. The principle involved is that the pure gas is first compressed above mercury in a graduated tube and the volumes corresponding to given pressures noted. Similar readings are then taken for the same gas after a small accurately measured amount of solvent has been introduced into the graduated tube. The difference between the two volumes at the same temperature and pressure, reduced to 1 kg. per sq. cm. and 1 ml. of liquid, represents the solubility of the gas in the given solvent.

Finally, attention should be called to the method of determination of gas solubility based on the principle that, for volatile solutes which obey the laws of Dalton and Henry, the amount which is carried away by an inert gas when known volumes are bubbled through solutions of known strength of volatile solute, can be used to measure the comparative solubilities in solvents of different concentrations. An example of this method is the determination of the solubility of ammonia in aqueous salt solutions by Abegg and Riesenfeld (1902). The very ingenious apparatus consists of a generator for developing a stream of H_2+O_2 from aqueous NaOH, by means of an electric current measured with the aid of a copper voltmeter, and the volume of gas thus determined. This was passed through a spiral in the vessel containing the ammonia solution of known concentration. The mixed gasses passing out of this were received in a third vessel containing 5 ml. of 0.01 *n* HCl. Electrodes were provided in this vessel and, by means of conductivity measurements, the point determined at which all of the HCl became saturated with NH_3. Since the volume of the H_2+O_2 required for this purpose was known, the partial pressure of the NH_3 in the mixture could be directly ascertained. Comparative determinations of the vapor pressure of the ammonia in water and a series of salt solutions made in this way were calculated to ammonia solubilities on the basis of the relation that, for two solutions of equal ammonia content, the ammonia pressure is reciprocally proportional to the solubility of the ammonia in them.

SPECTROGRAPHIC ANALYSIS [1]

Introduction.—The analysis of materials by a spectrographic method is dependent on the atomic excitation of the substance and the observation of the radiant energy produced by means of a spectroscope or spectrograph which separates this energy into an ordered arrangement of increasing wavelength or frequency of vibration. The success of the method is dependent on the ability to excite the molecule or atom and the intensity and character of the radiant energy produced. One might divide the subject of spectrographic analysis into qualitative and quantitative analysis, and also into the fields of emission and absorption analysis. From the standpoint of elemental analysis the division of Qualitative and Quantitative emission analysis is most important, although some mention will also be made of the application of absorption spectrographic analysis. In general it might be said that qualitative and quantitative spectrographic analyses are usually applied to the detection and estimation of minute amounts or traces of substances. The accuracy of a spectrographic quantitative analysis is seldom greater than $\pm 5\%$ of the amount of substance present and, as a rule, this represents a rather large error compared with the accuracy of chemical methods, except when the amount of substance or element present is very small.

The excitation of an atom by means of high temperature or electrical discharge results in the forcing of electrons from certain inner levels to outer levels or even completely out of the sphere of influence of the atom. The return of the electron to its original level or some other level and then from that level to another or its original level results in the emission of radiant energy which is definitely characterized or we might say quantized, in that it constitutes a definite voltage energy change which may be measured by the frequency or wavelength of the radiated energy. This radiated energy when observed in a spectroscope or spectrograph appears as a spectrum line and indicates not only the existence of the element but also the state of the atom (i.e. the number of electrons completely removed or the state of ionization). The number and intensity of the spectral lines are influenced by many factors. In some elements the excitation energy is concentrated in a limited number of possible electron jumps with the production of a rather simple spectrum (such as K or Hg), Fig. 501, whereas, in other elements the conditions in the atom may produce a scattering of the energy over a large number of possible electron jumps with the production of a very complicated spectrum (such as Fe or Mo).

The theoretical spectroscopist often indicates these differences in energy levels in volts, but for purposes of analysis it is more convenient to record them in the frequency or wavelength of radiant energy which is produced by this voltage change. The unit of wavelength (λ) in spectroscopy is usually the angstrom (A) (sometimes indicated by Å, A.U., or I.A.) which may be defined as 1 A = 1 meter $\times 10^{-10}$. Because of the importance of this unit and the large

[1] Chapter by Wallace R. Brode, Associate Professor of Chemistry, The Ohio State University.

number of accurate observations which are based on it, the actual unit of measure is not derived from subdivision of the meter but rather by the assignment to the red cadmium line the value 6438.4696 as the wavelength primary standard. The various units for the indication of wavelength or frequency values bear the following indicated relationships.

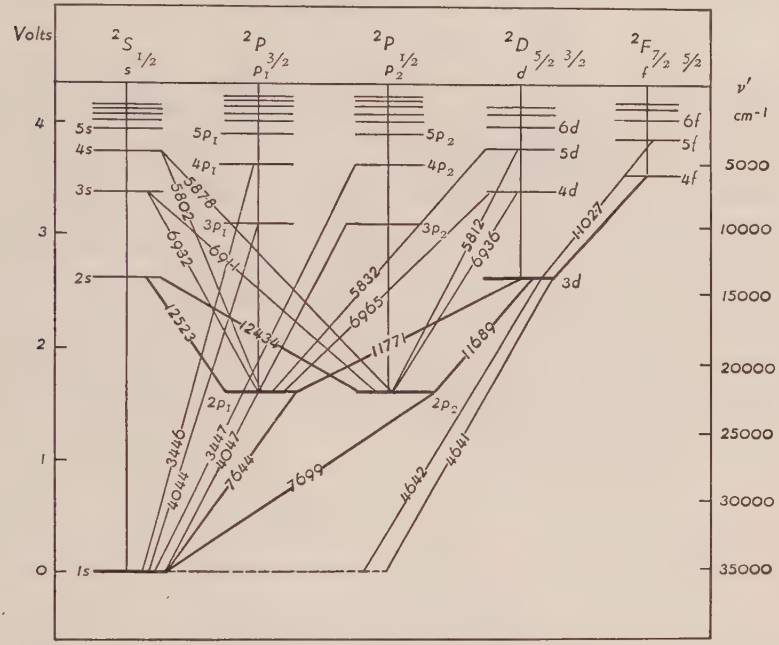

FIG. 501. Energy Level Diagram for Potassium (Numbers on lines between levels indicate the wavelength of the emitted energy.)

Wavelength (λ) (length of wave in a complete cycle).

1 A. (angstrom) $= 10^{-10}$ meters $= 1/6438.4696$ of the wavelength of the cadmium red line.

1 mμ $= 10$ A $= 10^{-9}$ meters.
1 μ $= 1000$ mμ $= 10{,}000$ A $= 10^{-6}$ meters.

Wavenumber (ν') oscillations per unit distance.

cm^{-1} = oscillations per cm.

Frequency (ν): Vibrations per unit time.

f (fresnel) = vibrations/seconds $\times 10^{12}$.

Relation between systems

$1/\lambda = \nu' = \nu/3$ (for example, 5000 A = 500 mμ = 20,000 cm^{-1} = 600 f).

The photographic range of radiant energy includes the spectral range of 2000 A to 14,000 A. This includes portions of the infra red, the visible region and portions of the ultraviolet.

Infra red above	7500 A
Red	7500 to 6000
Yellow	6000 to 5500
Green	5500 to 5000
Blue	5000 to 4000
Ultraviolet below	4000 A

It is interesting to note that the wavelength region of the visible in mμ units includes the numerical range from 400 to 750, while the frequency range for the same spectral range goes from 750 to 400 f. For the recording of spectral data, especially in connection with absorption and band spectra, it is more advisable to record in frequency or wavenumber, in that the data is usually capable of analysis into multiple band systems on a frequency basis. If a quartz spectrograph is used the dispersion is nearly linear for the spectral region when plotted on a frequency scale so that the accuracy of plotting or reading is approximately the same in all regions of the spectrum. With a grating spectrograph the data is observed on a linear or nearly linear dispersion based on the wavelength scale. For all spectrographic data involving line or emission spectra the data are recorded in wavelength in angstrom units, and for nearly all types of qualitative and quantitative analysis this is the only system with which one need be familiar.

APPARATUS

Spectrographic analysis involves rather complicated apparatus and requires a considerable capital outlay with regard to the cost of the equipment. The upkeep, however, is slight and once the apparatus has been properly adjusted and calibrated the technical knowledge for the preparing of the photographic data and the interpretation of the data is such that much of the work can be done by technical assistance in the laboratory. The type of spectrograph necessary for analytical work will depend on the composition of the samples to be analyzed, the degree of accuracy expected and the speed with which the analysis must be made. For many of the non ferrous metals giving simple spectra, such as Zn, Cd, Hg, Ag, Au and the like a high dispersion spectrograph is not necessary. The usual type of Cornu prism instrument (Fig. 502) with a dispersion of about 10 inches from 7000 to 2000 A is quite satisfactory, and in some cases a slightly lower dispersion such as given by a small model Littrow or the Cornu instruments may be sufficient for purposes of analysis (Figs. 503 and 504).

For the analysis of ferrous metals, W, Mo, U, Pt and elements giving large numbers of lines it may be necessary to use an instrument capable of giving sufficient dispersion to separate the spectrum lines. For this purpose one usually employs a grating instrument or a prism instrument of the Littrow type (Figs. 505a, b and 506).

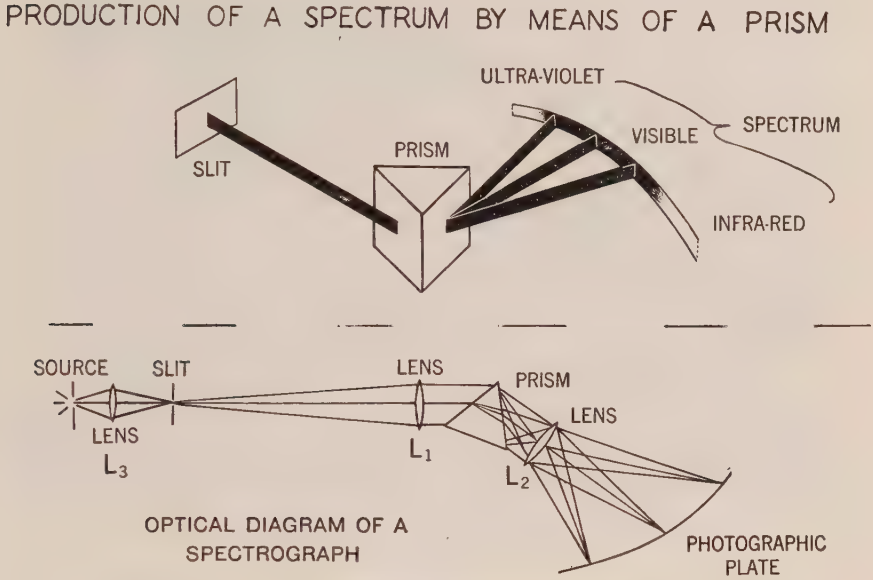

FIG. 502. Production of a Spectrum by a Prism and an Optical Diagram of a Prism Spectrograph (drawing is not to scale).

Both of these instruments (Cornu and Littrow) employ the same optical principles as indicated in the illustrating figures (Figs. 502 and 505). The prism spectrograph or spectroscope utilizes the optical principles of refraction and dispersion, i.e., the bending of a light beam by a prism and the fact that

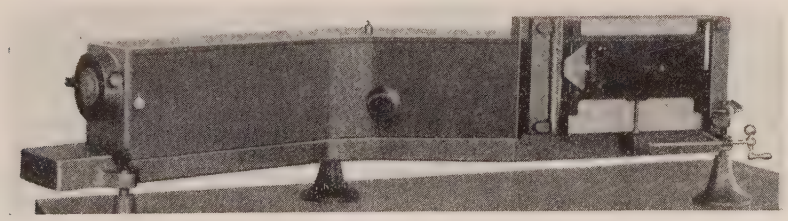

FIG. 503. Bausch and Lomb Spectrograph Medium Size (4×10 in spectrum plate).

the degree of refraction is influenced by the wavelength or frequency of the incident light or radiant energy. For most spectrographs the prism and lens systems are made from quartz because of its transmission of radiant energy

over the entire spectral region to which the photographic plate is sensitive. The light which is focused on the slit of the instrument is collected by a collimating lens so as to project a parallel beam through the prism. After refraction

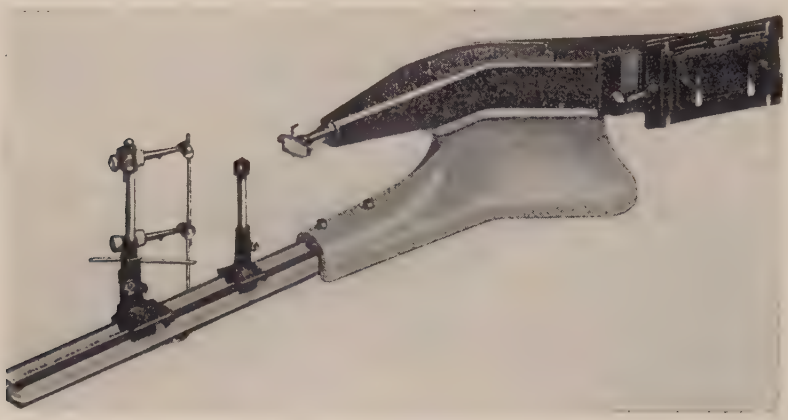

Fig. 504. Hilger Spectrograph (Small Size instrument No. E 484).

by the prisms and the dispersion of the beam the light is focused by a second lens on the plate or eyepiece. It should be noted that in the Littrow instrument a single lens serves both as focusing and collimating, and the prism is only 30° with a mirror back so that the light beam travels half way through what

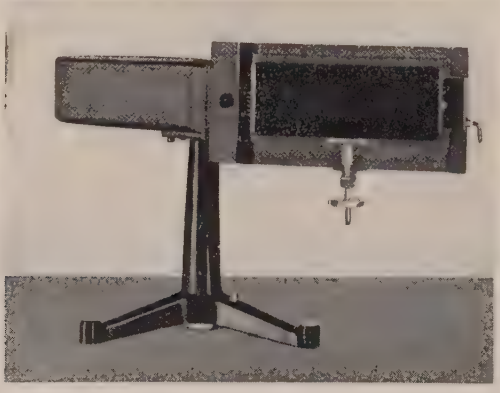

Fig. 505a. Small Littrow Spectrograph. (Bausch and Lomb.)

would be a 60° prism if it were continued, and then is reflected back so that the beam passes through the prism twice. In view of the economy of quartz pieces, as well as size of the instrument, the Littrow construction is particularly well suited for the larger instruments with high dispersion.

The illumination of the slit of the spectrograph may be varied to suit the conditions of the analysis. While the common practice is to focus the image of

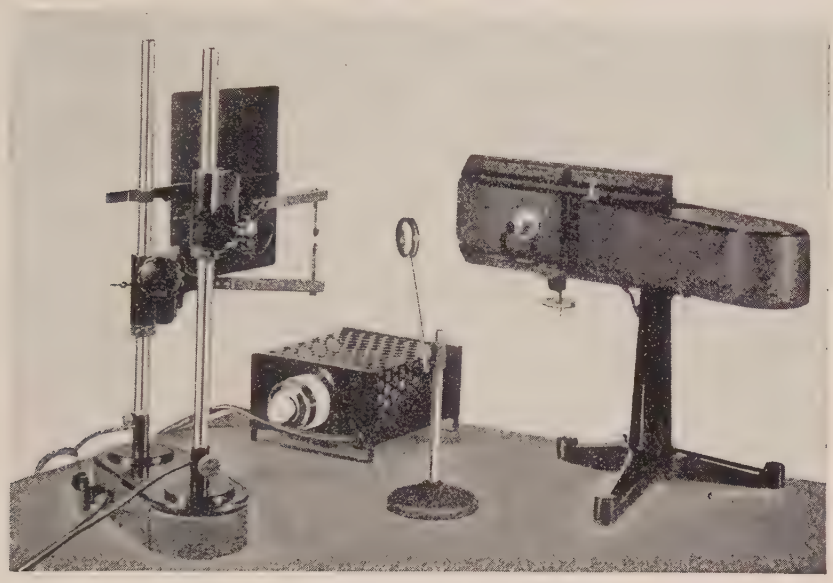

FIG. 505b. Illumination System for Small Littrow Spectrograph. (Bausch and Lomb.)

the source on the slit, and so diaphragm the slit with a wedge or Hartmann diaphragm (Fig. 507) as to cut off undesirable illumination from certain portions

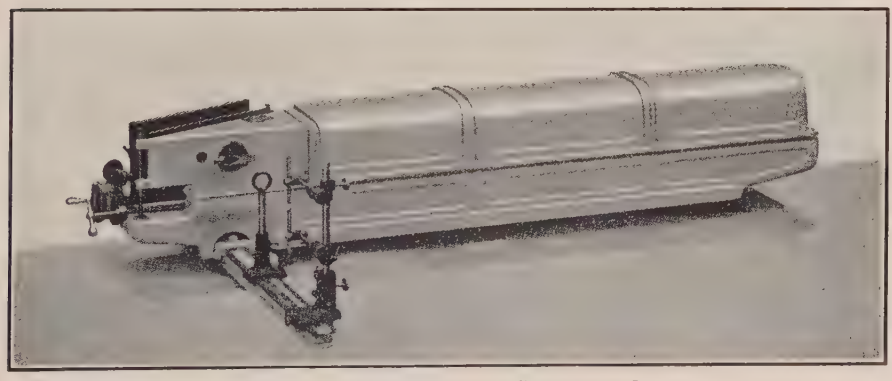

FIG. 506. Hilger Littrow Spectrograph.

of the source, there may be occasions where it is desirable to use a large amount of the sample so as to obtain an average analysis of the sample. In this latter case the condensing lens may be entirely eliminated. If it is still desirable

to diaphragm part of the source one may use screen absorbers near the focusing lens to reduce the total intensity. For certain types of analysis it is desirable to have the slit illuminated uniformly along its entire length; this is especially true in the use of the logarithmic sector method or the step slit method of analysis. This can be easily accomplished by the use of a long focus lens placed as near the slit as is possible and placing the light source in such a position that the image of the source is focused on the collimating lens of the spectrograph (L_1—Fig. 502). If one attaches a rectangular diaphragm to this lens it is possible to eliminate the undesirable portions of the spectrum. This system of illumination does not make full use of the resolving power of the instrument, but in most cases this is not necessary and the reduction in the light intensity is not a serious handicap in most analytical work since the increased exposure provides for a more thorough sampling of the material to be analysed.

Fig. 507. Wedge and Hartmann Diaphragm for Spectrograph Slit.

LIGHT SOURCES

Flame.—Flame sources are useful for rough qualitative tests which may be applied in addition to visual color tests of the flame, for such elements as Cu, Na, Li, K, Ca, Sr, Ba, etc. The temperature and constancy of the flame are not very satisfactory for the spectrographic analysis and with the exception of the alkali metals, those elements which give colored flames, usually do so as compounds with certain anions (i.e. $CaCl^+$, $CuCl^+$, etc.), the color being caused by the band spectrum of the diatomic or triatomic molecule rather than by the simple element. A quantitative method has been described, however, for the estimation of boron by the color of the green flame produced by the burning of methyl borate, by which relatively small amounts of boron may be detected and estimated quantitatively.

Arc.—The two most important methods of atomic excitation for spectrographic analysis are by means of the electric arc and the electric spark. It is difficult to draw a sharp dividing line between these methods especially when high voltage arcs of 2 to 3 thousand volts are commonly used. In general, however, the arc sources are confined to the use of current densities of 3 to 5 amps. and 50 to 200 volts (Fig. 508). The arc constancy can be improved by the inclusion in the circuit of a reactance (such as the primary coil of a 1 KVA transformer in which the secondary circuit has been shorted). While the current source may be from 120 to 220 volts (DC) the actual drop across the arc gap may be only 40 to 60 volts, due to the use of a resistance in the circuit.

One usually uses rods of the sample about $\frac{1}{4}$ inch in diameter. Metals are usually worked by using pairs of rods of the material. For non-conducting substances and small quantities, as well as solutions, carbon rods are usually used. In such cases the lower carbon is usually cupped so as to take the sample. The lower carbon may be the positive or negative electrode, depending on the substance for which the analysis is being made and the spectral characteristics desired. The commercially available carbon comes in several grades, of which the spectrographic and high purity types are suitable for most analyses. The highest purity material is usually free from nearly all impurities with the excep-

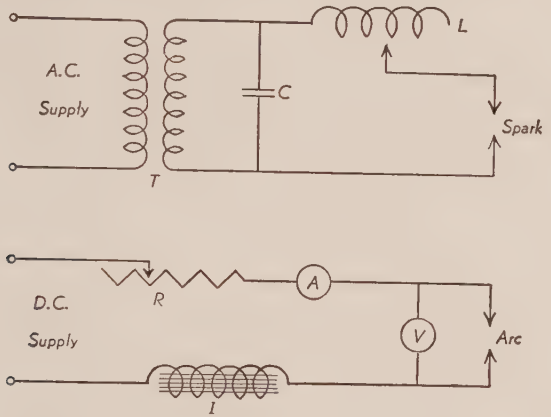

FIG. 508. Electrical Diagram for Spark and Arc Sources. T = Transformer 10,000 to 20,000 V.; L = Self Inductance 0.25 millihenry; C = Capacity, 0.005 microfarads: D.C. Source 110–220 volts; R = Resistance; Arc current 2 to 5 amps., 40–70 volts; I = Reactance.

tion of a trace of Si. Less expensive rods usually contain minute traces of Fe, Al, Ca, Cu, Ti, Mg, and V. These may not interfere with the analysis or they can be removed by purification. One method of purification involves the soaking of the carbon in HCl and HNO_3. A recently described method of purification which yields excellent results is effected by heating the carbon as a resistance rod to a temperature of about 2400° in a vacuum furnace. This treatment seems to be effective in the removal of nearly all of the impurities from carbon rods containing a considerable amount of impurity. In some cases it is possible to use pure metal electrodes, such as copper as the holder for the substance to be examined. Duffendack and Wolfe have recommended the use of a high voltage arc using 2.5 amps. at 2500 volts. It is claimed that this procedure reduces if not entirely eliminates background and that in the examination of salts the thin layer of salt solution on the carbon rods, formed by the evaporation of a drop of solution on the rods is sufficient to prevent the production of the carbon-cyanogen bands. The temperature of the electrodes remains very low so that low-melting alloys may be conveniently analysed by this method.

Spark.—The change in electrical excitation from arc to spark results in an alteration in the spectrum with regard to intensities of lines, production of

new lines and the elimination of arc lines. The usual electrical system is indicated in Fig. 508. The use of a self inductance changes the spark characteristics with a reduction in the intensity of air lines (from O and N) and in some cases may so alter the characteristics of the spark so that it may appear more like an arc spectrum. The self inductance does help stabilize the conditions, and it is to be recommended in spectrographic analysis, especially where it may be desirable to have reproducible conditions. There appears to be a satisfactory medium between the condensed and oscillatory spark since the factor determining the number of oscillations is a function of the product of the capacity of the condenser system and the inductance of the self inductance.

Since the equipment available in each laboratory will differ in some detail and the conditions of excitation must be varied for different elemental analysis, it is not practical to give in this limited discussion any more detailed descriptions of arc and spark procedures. Nearly all articles on spectrographic analysis indicate with some detail the method of excitation and in attempting to duplicate such methods it is advisable to follow the excitation procedure as closely as possible. In the spectrographic analysis of solutions the sample may be applied to a carbon electrode and arced or sparked or a spark discharge may be effected by using the solution as one electrode and a carbon, gold or copper rod as the other electrode.

Other Light Sources.—For the analysis of gases one usually uses a gas discharge tube with a high frequency high voltage current. The presence of impure gases may often interfere with, or even completely eliminate, the lines of certain substances so that the method may not be entirely satisfactory. For the purpose of providing a background of nearly continuous radiation for the observation of absorption spectra one may use the incandescent tungsten filament for the visible and near ultraviolet. The ultraviolet range may be extended a little by the use of a special bulb of correx glass or a quartz window in the glass bulb. For an extension in the ultraviolet to the limit of the gelatin emulsion one may use an under water spark from a tesla coil or a hydrogen discharge, both of which give a continuous spectrum, without spectral lines over nearly the entire photographic range from 2000 to 8000 A. For some types of absorption work, especially where the bands are broad, satisfactory results can be obtained by using an arc or spark between tungsten, iron or nickel electrodes.

Spectrographic Standards.—In the definition of dispersion measurement terms it was indicated that rather than defining wavelength in angstrom units as a ten thousand millionth of a meter it was defined as 1/6438.4696 part of the wavelength of the cadmium red line, and this line is known as the primary standard. As further guides in the measurement of the wavelength of unknown lines a number of secondary standards have been designated and their wavelength accurately measured. These secondary standards include some 217 iron, 9 copper, 3 silicon, 2 nickel and 25 neon lines. The almost universal use of the iron spectrum as a means of identification and comparison of other spectra has resulted in the accurate determination of the wavelength values of some three hundred and eighty-four additional lines which are known as tertiary standards. The wavelength values of unknown lines can be accurately determined by measurement of the spacing between the unknown line and selected standard lines and the application of the Hartmann formula to these data.

For the identification of the unknown element in a spectrographic analysis, a number of special tables and photographic charts have been prepared. These tables and charts may be subdivided and classified in accordance with their method of preparation and use.

1. Spectrum lines in accordance with the element. The most complete table (in so far as it has been finished) is the Kayser-Konen Handbuch (Vol. 7 and 8), in which the elements up to Nd in an alphabetical arrangement have been covered. It is of course impossible to cover adequately or report all of the possible lines of an element that might be produced by extremely long exposures or by increasing the ionization state. The Kayser collection presents, however, the most complete assembly of spectral line values for these elements that has as yet been published. It is hoped that within a few years a more complete set of tables can be published from data which is being collected by G. R. Harrison of the Massachusetts Institute of Technology, and for which over two million line measurements have been made with an accuracy of within .001 A. Kayser published in 1910–1912 two volumes (Vol. 5 and 6 of the Kayser Handbuch der Spectroscopie) covering available data on the elements at that time. Other available lists included the data published by Exner and Haschek, the Tables Annuelles des Constantes and miscellaneous original research publications. For the aid of the qualitative spectroscopist condensed tables of the more intense lines have been published, the most convenient of these is to be found in the International Critical Tables. (This data is also reprinted in the Handbook of Chemistry and Physics.) It has been shown that upon dilution of elemental concentration of a known substance in an arc or spark, that the intensities of the spectral lines due to that element will be reduced and that the weaker lines will gradually fade out through lack of sufficient intensity to affect the photographic emulsion. The last lines to disappear are known as the persistent lines or the Raies Ultimes. These lines have been determined for nearly all of the known elements, together with their spectral class (Table I). In the examination of a spectrogram of an unknown sample for certain elements, the absence of the Raies Ultimes of that element in the spectrogram is usually sufficient proof for the absence of the element.

2. A second type of spectral tabular data involves the arrangement of lines in accordance with wavelength values rather than by elements. This type of arrangement is particularly useful in the qualitative identification of unknown elements present in the sample. The best available table of this type is that of Kayser (Hauptlinien). There are a number of more condensed tables such as the 10,000 line table in the Lange Handbook, Twyman (second edition), Löwe, Scheibe, etc. A similar table to some of these has been prepared directly from more extended tables (Table II). This table is confined to the relatively more intense lines and especially those of the arc spectrum. It is of course difficult to know where to limit a table of this type since one may not be sure in the identification of a single line as to whether it is a weak uncharted line of the element present in greatest amount or the strong line of the element present in weak amounts. For this reason it is usually customary to verify the presence of elements by the identification of several lines of the element in question. In Fig. 509, which shows the spectra of brass and copper samples, one can note the procedure in the identification of impurity or alloying elements. The method of taking photographs of comparison or pure samples adjacent

TABLE I

PERSISTENT ARC LINES OF THE ELEMENTS

(I, II etc. indicate atomic states; [1] indicates the most persistent lines)

Ag I	[1]3280.7A	Ca I	4456.6	Er I	3692.7	La I	5455.1
	3382.9	Ca II	[1]3933.7		3906.3		[1]5930.6
Ag II	2246.4		3968.5	Eu I	4129.7		6249.9
	2437.8	Cb I	[1]4059.0		4205.0	La II	[1]3949.1
Al I	3082.2		4079.7	Fe I	[1]3719.9		4077.4
	3092.7		4101.0		3737.1		4123.2
	3092.9		4123.9		3745.6	Li I	3232.7
	3944.0		4137.1		3748.3		[1]6707.9
	[1]3961.5	Cb II	[1]3094.2		3745.9	Lu I	4518.5
Al II	1671.0		3130.8	Fe II	[1]2382.0	Lu II	2894.9
	1856.0		3163.4		2395.6		2911.4
	1858.1		3195.0		2404.9		3397.0
	1862.5		3225.5		2410.5		3472.5
Al III	1854.7	Cd I	[1]2288.0		2413.3		3554.4
	1862.9		3403.7	Ga I	4033.0	Mg I	[1]2852.1
As I	1889.9		3466.2		[1]4172.0		3829.4
	1936.9		3510.5	Gd I	3646.2		3832.3
	1972.0	Cd II	[1]2144.4		3768.4		3838.3
	2288.1		2265.0	Ge I	2651.2	Mg II	[1]2795.5
	2349.8	Ce II	4012.4		2651.6		2802.7
	2780.2		4040.8		3039.1	Mn I	[1]4030.8
	2860.5		4165.6		3269.5		4033.1
Au I	[1]2427.9		4186.6		4226.6		4034.5
	2675.9	Co I	[1]3453.5	Hf I	2898.2	Mn II	[1]2576.1
B I	2496.8		3465.8		2904.4		2593.7
	[1]2497.7		3529.8		2916.5		2605.7
B II	1362.5	Co II	[1]2286.2		2940.8	Mo I	[1]3798.3
	3452.3		2307.8		3072.9		3864.1
Ba I	5424.6		2378.6		4093.2		3903.0
	5519.1		2388.9	Hf II	2513.0	Mo II	[1]2816.2
	[1]5535.5	Cr I	[1]4254.3		2516.9		2848.2
	5777.7		4274.8		2641.4		2871.5
Ba II	[1]4554.0		4289.7		2773.4		2891.0
	4934.1		5204.5		2820.2		2909.1
Be I	[1]2348.6		5206.0		3134.7	Na I	3302.3
	3321.0		5208.4	Hg I	[1]1849.6		3302.9
	3321.1	Cr II	[1]2835.6		2536.5		5890.0
	3321.4		2843.3		3650.2		5895.9
Be II	[1]3130.4		2849.8		3654.8	Nd I	3951.2
	3131.1		2855.7		3662.9		4177.3
Bi I	2061.7		2860.9	Hg II	1649.8		4303.6
	2276.6	Cs I	[1]8521.2		1942.3	Ni I	[1]3414.8
	2780.5		8943.6	Ho I	3748.2		3493.0
	2809.6		4555.3		3891.0		3515.1
	2898.0		4593.2	Ho II	2936.8		3524.5
	2938.3	Cu I	[1]3247.5	In I	4101.8	Ni II	2253.9
	2989.0		3274.0		[1]4511.3		2264.5
	[1]3067.7	Cu II	[1]2136.0	Ir I	2849.7		2270.2
C I	[1]2478.6		2192.3		2924.8		[1]2287.1
C II	1334.5		2247.8		[1]3220.8	Os I	3262.3
	1335.7	Dy I	4000.5		3437.1		3267 9
	4267.0		4046.0		3513.7		3301.6
	4267.3		4078.0	K I	4044.2		3752.5
Ca I	[1]4226.7		4168.0		4047.2		3782.2
	4454.8		4211.7		[1]7664.9	P I	1774.8
	4455.9	Er I	3499.1		7699.0		1782.7

TABLE I. *Continued*

P I	1787.5	Ru I	3436.7	Sn I	4524.7	V I	3183.4
	2136.8		[3]3499.0	Sr I	[1]4607.3		3184.0
	2149.8		3596.2		4832.1		3184.0
	2536.4	Ru II	2678.7		4872.5		[3]3185.4
	2554.0		2692.1		4962.3	V II	[3]3093.1
Pb I	[1]2170.0		2712.4	Sr II	[1]4077.7		3102.3
	2833.1		2945.7		4215.5		3110.7
	3639.6		2965.6	Ta I	[3]3311.1		3118.4
	3683.5		2976.6		3318.9		3125.3
	4057.8	Sa I	4390.9		3406.7	W I	[1]4008.8
	1682.4		4424.4	Tb I	3509.2		4294.6
Pb II	[1]2203.6		4434.3		3561.8		4302.1
Pd I	[3]3404.6	Sb I	2068.4		3848.8	W II	2397.1
	3421.2		2175.9		3874.2		2589.2
	3517.0		2311.5	Te I	2142.8		3613.8
	3609.6		2528.5		2383.3	Y I	4643.7
	3634.7		2598.1		2385.8		[1]4674.8
Pd II	2488.9		3232.5		2530.7	Yt II	[3]3710.3
	2498.8		3267.5		2769.7		3774.3
	2505.7	Sc I	3907.5	Th I	3538.8		3788.7
	2658.7		[3]3911.8		3601.1	Yb I	3289.4
	2854.6	Sc II	[3]3613.8		4019.1		3694.2
Pr I	4062.8		3630.8	Th II	3290.6		3988.0
	4179.4		3642.8	Ti I	3635.5	Zn I	[1]2138.5
	4189.5	Se I	1960.2		3642.7		3282.3
	4225.3		2039.7		[3]3653.5		3302.6
Pt I	2659.4		2062.6		4981.7		3344.5
	2830.3		[1]4730.9		4991.1	Zn II	[1]2025.5
	2929.8		4739.1		4999.5		2061.9
	2998.0		4742.3		5007.2	Zr I	[3]3519.6
	[3]3064.7	Si I	2506.9		5014.3		3547.7
Ra I	[1]4825.9		2516.1	Ti II	[3]3349.0		3601.2
Ra II	[3]3814.4		2528.5		3361.2		4687.8
	4682.2		[1]2881.6		3372.8		4710.1
Rb I	4201.8		3905.5		3383.8		4739.5
	4215.6	Si II	1526.8	Tl I	3775.7		4772.3
	[1]7800.3		[1]1533.6		[1]5350.5		4815.6
	7947.6	Sn I	2840.0	Tu I	3462.2	Zr II	[3]3392.0
Rh I	3323.1		2863.3		3761.3		3438.2
	3396.8		3009.1		3761.9		3496.2
	[3]3434.9		3034.1	U I	3552.2		3572.5
	3658.0		3175.0		3672.6		
	3692.4		3263.3		4241.7		

to the unknown sample provides a rapid procedure for the identification of impurity lines and the approximate identification of the wave length value, especially if the adjacent spectrum be iron or some other element which gives a large number of lines and for which accurate photographic charts are available. In connection with the spectrographic program at the Massachusetts Institute of Technology it is hoped that a table of 100,000 or 200,000 lines arranged in accordance with the wavelength of the line will be published.

The photographic charts available are usually of the iron spectrum although there are charts for some other elements such as Cu and Ne. A number of elements are available in extremely high states of purity for the purpose of taking comparison spectra. The most complete photographic set of data avail-

TABLE II

Arc Lines of the Elements

(arranged according to wavelength values, I, II indicate atomic states)

Zn II	2025.5A	As I	2349.8	Pd II	2505.7	Pt	2650.9
Se I	2039.7	Pd	2351.4	Ag	2506.7	Be	2650.9
Bi I	2061.7	Sn	2354.8	Si	2506.9	Ge I	2651.2
Zn II	2061.9	Co	2363.8	Ni	2510.9	Ge I	2651.6
Se I	2062.6	Al	2367.1	Hf II	2513.0	Al I	2652.5
Sb I	2068.4	As	2369.7	Si I	2514.3	Pt I	2659.4
Cu II	2135.9	Cu I	2369.9	Si I	2516.1	Ag	2660.4
P I	2136.8	As	2370.8	Hf II	2516.9	Sn	2661.3
Zn I	2138.5	Al I	2373.1	Si I	2519.2	Pb	2663.2
Te I	2142.8	Co II	2378.6	Co	2519.8	Cr	2666.0
Cd II	2144.4	Fe II	2382.0	Fe	2522.9	Al II	2669.2
P I	2149.8	Te I	2383.3	Si I	2524.1	Cr II	2671.8
Pb I	2170.0	Te I	2385.8	Fe I	2524.3	Mo	2672.8
Sb I	2175.9	Co II	2388.9	Cs	2525.6	Au I	2676.0
Pb II	2203.6	Pb	2393.8	Fe I	2527.4	Cr	2677.2
Cu	2227.8	Ni	2394.6	Ba II	2528.5	V	2678.6
Cu	2230.1	Fe II	2395.6	Si I	2528.5	Ru II	2678.7
Cu	2242.6	W II	2397.1	Sb I	2528.5	Cr	2678.8
Cu	2247.0	Fe II	2404.9	Co I	2529.0	Mo	2684.1
Cu II	2247.8	Fe	2406.7	Te I	2530.7	Pt	2702.4
Ag	2248.7	Co I	2407.3	P I	2535.6	Pt	2705.9
Ni II	2253.9	Fe II	2410.5	Hg I	2536.5	V	2706.2
Te	2255.5	Ag	2411.4	Mo	2538.5	Sn	2706.5
Te	2259.0	Ag	2413.2	Ni	2545.9	Ge	2709.6
Al I	2263.5	Fe II	2413.3	P	2553.3	V	2715.7
Ni II	2264.5	Ni	2416.1	Zn II	2558.0	Pt	2719.0
Cd II	2265.0	Pd	2424.5	Fe II	2562.5	Fe	2719.0
Te	2265.5	Pd	2426.9	Al II	2568.0	Fe I	2721.0
Al I	2269.1	Mn II	2427.8	Zr	2571.4	Fe II	2739.6
Ni II	2270.2	Mn II	2427.9	W	2572.3	Fe II	2743.2
Bi I	2276.6	Au I	2427.9	Cd II	2573.0	As I	2745.0
Co II	2286.2	Sn	2429.5	Al I	2575.1	Fe II	2746.5
Ni II	2287.1	Pd	2430.9	Mn II	2576.1	Au	2748.3
Cd I	2288.0	Pd	2433.1	Pb	2577.3	Cd II	2748.7
As I	2288.1	Si I	2435.2	Co	2580.3	Fe I	2749.3
Ni	2290.0	Pd	2435.3	Fe	2585.9	Cr II	2750.7
Pd	2296.5	Mn II	2437.5	Ge	2593.6	W	2764.3
C	2296.8	Ag II	2437.8	Mn II	2593.7	Cr II	2766.5
La	2297.8	Ni	2437.9	Sb I	2598.1	Ag	2767.5
Ba II	2304.2	Ag	2447.9	Fe II	2598.4	Fe I	2767.5
Co II	2307.9	Mn II	2452.5	Fe II	2599.4	Tl I	2767.9
Ag	2309.5	As	2456.5	Mn II	2605.7	Te	2769.7
Sb I	2311.5	Ag	2473.9	Fe II	2607.1	Sb I	2769.9
Co I	2311.6	Pb	2476.4	Fe II	2611.9	Hf II	2773.4
Cd II	2312.9	C II	2478.6	Pb	2613.7	Mg I	2776.7
Ni	2316.0	Fe	2483.3	Fe II	2613.8	Mg I	2778.3
Ag	2317.0	Fe I	2484.2	Pb	2614.2	Mg I	2779.9
Ag	2320.2	W	2488.8	Pt	2628.0	As I	2780.2
Ag	2324.6	Pd II	2488.9	Fe II	2628.3	Bi I	2780.5
Ag	2331.4	As	2492.9	Cs	2630.6	Mg I	2781.4
Fe II	2332.8	Be	2494.4	Fe II	2631.1	Mg I	2783.0
Ba II	2335.3	Be	2494.9	Al II	2631.6	Mg II	2790.8
Fe II	2343.5	B I	2496.8	Ba	2634.8	Mg II	2795.5
Ba II	2347.6	B I	2497.7	Hf II	2641.4	Mg II	2798.0
Fe II	2348.1	Pd II	2498.8	Au	2641.5	Mn I	2798.3
Be I	2348.6	Zn II	2502.0	Be	2650.3	Mn I	2801.1

TABLE II. *Continued*

Au	2802.2	Bi I	2993.3	V I	3183.4	Ti II	3361.2
Mg II	2802.7	Pt I	2998.0	V I	3184.0	Ti I	3371.5
Bi I	2809.6	Ni I	3002.5	V I	3185.4	Ti II	3372.8
Mo II	2816.2	Ni I	3003.6	Mo I	3194.0	Ti I	3377.6
Al II	2816.2	Sn I	3009.1	Cb II	3195.0	Ni I	3380.6
Hf II	2820.2	Ni I	3012.0	Y II	3195.6	Ag I	3382.9
Pb	2823.2	Cr	3014.9	Ti I	3199.9	Ti II	3383.8
Pt I	2830.3	Fe I	3020.7	Ir I	3220.8	Zr	3387.9
Pb I	2833.1	Fe I	3021.1	Cb II	3225.5	Co I	3388.2
Cr II	2835.6	Bi	3024.6	Sb I	3232.5	Zr	3388.3
Cd I	2836.9	Sb I	3029.8	Li I	3232.7	Zr II	3392.0
Sn I	2840.0	Sn I	3034.1	Ti II	3234.5	Ni I	3393.0
Cr	2840.0	Ni I	3037.9	Ti II	3236.6	Co I	3395.4
Cr II	2843.3	Ge I	3039.1	Ti II	3239.0	Rh I	3396.8
Mo II	2848.2	In I	3039.4	Ti II	3242.0	Lu II	3397.0
Ir II	2849.7	Co I	3044.0	Pd I	3242.7	Re I	3399.3
Cr II	2849.8	Fe I	3047.6	Cu I	3247.6	Hf	3399.8
Mg I	2852.1	Ni I	3050.8	Cd II	3250.3	Cd I	3403.7
Mo	2853.2	Ni I	3054.3	Cd I	3252.5	Pd I	3404.6
Pd II	2854.6	Ni I	3057.7	In I	3256.1	Co	3405.1
Cr II	2855.7	Os I	3058.7	Cd I	3261.1	Ta I	3406.9
As I	2860.5	Pt I	3064.7	Os I	3262.3	Co I	3409.2
Cr II	2860.9	Ti II	3066.4	Sn I	3262.3	Zr II	3410.3
Sn I	2863.3	V	3066.4	Sb I	3267.5	Co I	3412.3
Mo II	2871.5	V	3067.1	Os I	3267.9	Ni I	3414.8
Pb	2873.3	Bi I	3067.7	Ge I	3269.5	Pd I	3421.2
Sb I	2877.9	Ti II	3072.1	Zr II	3273.1	Pd I	3433.4
Si I	2881.6	Hf	3072.9	Cu I	3274.0	Ni I	3433.6
Mo II	2891.0	Ti II	3075.2	Zr II	3279.3	Rh I	3434.9
V	2891.7	Zn I	3075.9	Ag I	3280.7	Ru I	3436.7
V	2892.7	Al I	3082.2	Zn I	3282.3	Ir I	3437.0
V	2893.3	Ti II	3088.0	Sn	3283.5	Ni I	3437.3
Lu II	2894.9	Mg I	3091.1	Zr I	3284.7	Zr II	3438.2
Bi I	2898.0	Al I	3092.7	Th II	3290.6	K	3440.4
Hf I	2898.3	Al	3092.9	Th II	3300.5	Fe I	3440.6
As I	2898.7	Mg I	3093.1	Os I	3301.6	Fe I	3441.0
Lu II	2900.3	V II	3093.1	Pd	3302.1	Pd	3441.4
Hf I	2904.4	Cb II	3094.2	Na I	3302.3	Mn II	3442.0
V	2908.8	Mg I	3096.9	Zn I	3302.6	Ni I	3446.3
Os	2909.1	V II	3102.3	Na I	3302.9	Mo	3447.1
Mo II	2909.1	V II	3110.7	Ta I	3311.1	K	3447.4
Lu II	2911.4	V II	3118.4	Th	3313.7	B II	3452.3
Hf I	2916.5	Mo	3122.0	Ta I	3318.9	Co I	3453.5
V	2924.0	Au	3122.8	Be I	3321.0	Mn II	3460.3
Ir I	2924.8	V II	3125.3	Be I	3321.1	Pd	3460.8
Mg II	2928.7	Hg I	3125.6	Be I	3321.3	Tu I	3462.2
Pt I	2929.8	Be II	3130.4	Ti II	3322.9	Co I	3462.8
Mn II	2933.1	Cb II	3130.8	Rh I	3323.1	Sr II	3464.5
Mg II	2936.5	Be II	3131.1	Sn	3330.6	Re I	3464.7
Ho II	2936.8	Hg I	3131.6	La II	3337.5	Co I	3465.8
Bi I	2938.3	Hg I	3131.8	Ti II	3341.9	Cd I	3466.2
Hf I	2940.8	Mo I	3132.6	Zn I	3345.0	Cd I	3467.7
Ru II	2945.7	Ir I	3133.3	Zn I	3345.5	Lu II	3472.5
Mn II	2949.2	Hf II	3134.7	Ti II	3349.0	Co I	3474.0
Ru II	2965.6	Ca II	3158.9	Ti II	3349.4	Mn II	3474.0
Hg I	2967.3	Cb II	3163.4	Sn	3352.3	Fe I	3475.5
Ru II	2976.6	Ti II	3168.5	Ti I	3354.6	Zr	3481.2
Cd I	2980.6	Mo I	3170.3	Zr II	3357.3	Pd I	3481.2
Fe I	2983.6	Sn I	3175.0	Mo I	3358.1	Mn II	3482.9
Bi I	2989.0	Ca II	3179.3	Cb I	3358.4	Mn II	3488.7

TABLE II. *Continued*

Fe I	3490.6	Hg I	3662.9	Fe I	3886.3	Th	4116.8
Ni I	3493.0	Hg I	3663.3	Ho I	3891.0	Co I	4118.8
Zr II	3496.2	U	3670.1	Ba II	3891.8	Co I	4121.3
Ru I	3499.0	Pb	3671.5	Ti II	3900.5	La II	4123.2
Er	3499.1	U I	3672.6	Mo I	3903.0	Cb I	4123.9
Ba I	3501.1	Pb I	3683.5	Si I	3905.5	V I	4128.1
Co I	3502.3	Ti II	3685.2	Er I	3906.3	Eu II	4129.7
Rh I	3502.5	Pd	3690.4	Sc I	3907.5	Ba II	4130.7
Tb I	3509.2	Rh I	3692.4	Sc I	3911.9	V I	4132.0
Ir I	3513.7	Er I	3692.7	Pt	3923.0	Li I	4132.4
Ni I	3515.1	Yb I	3694.2	Ca II	3933.7	Ce	4133.8
Pd I	3517.0	Zr	3698.2	Al I	3944.0	V I	4134.5
Tl I	3519.2	Rh I	3700.9	La II	3949.1	Cb I	4137.1
Zr I	3519.6	Y II	3710.3	Nd I	3951.2	Ce	4137.6
Ni I	3524.5	Fe I	3719.9	Ti I	3956.3	Ce	4165.6
Co I	3526.9	Fe I	3722.6	Ti I	3958.2	Dy I	4168.0
Rh I	3528.0	Ru I	3726.9	Rh I	3958.9	Pb	4168.0
Co I	3529.8	Ru I	3728.0	Al I	3961.5	Ga I	4172.1
Th	3538.8	Fe I	3734.9	Ti I	3964.3	Hf	4174.3
Zr I	3547.7	Fe I	3737.1	Pt	3966.4	Nd I	4177.3
U I	3552.2	Pb	3740.0	Ca II	3968.5	Y II	4177.5
Pd I	3553.1	Th	3741.2	Ti I	3981.8	Pr I	4179.4
Lu II	3554.4	Fe I	3745.6	Yb I	3988.0	Ce II	4186.6
Ce II	3560.8	Fe I	3745.9	La II	3988.5	Pr I	4189.5
Tb I	3561.8	Ho I	3748.2	Ti I	3989.8	Rb I	4201.8
Fe I	3570.1	Fe I	3748.3	Co I	3995.3	Eu I	4205.0
Zr II	3572.5	Fe	3749.5	Ti I	3998.6	Rh I	4211.1
Sc II	3572.6	Os I	3752.5	Dy I	4000.5	Dy I	4211.7
Pb	3572.7	Fe I	3758.2	W I	4008.8	Ag I	4212.0
Cr I	3578.7	Ti II	3759.3	Ce II	4012.4	Sr II	4215.5
Nb I	3580.3	Tu I	3761.3	Th I	4019.1	Rb I	4215.6
Sc II	3581.0	Tu I	3761.9	Sc I	4020.4	Pr I	4225.3
Fe I	3581.2	Fe I	3767.2	Sc I	4023.7	Ge I	4226.6
Ru I	3593.0	Gd I	3768.4	Mn I	4030.8	Ca I	4226.7
Cr I	3593.5	Y II	3774.3	Ga I	4033.0	U I	4241.7
Ru I	3596.2	Tl I	3775.7	Mn I	4033.1	Sc II	4246.9
Rh	3596.2	Hf	3777.6	Mn I	4034.5	Cr I	4254.3
Y II	3600.7	Os I	3782.2	Ce II	4040.8	Os I	4260.9
Th I	3601.1	Y II	3788.7	K I	4044.2	C II	4267.1
Zr I	3601.2	Mo I	3798.3	Fe I	4045.8	C II	4267.3
Cr I	3605.3	Ru I	3798.9	Dy I	4046.0	Fe I	4271.8
Pd I	3609.6	Rh I	3799.3	Hg I	4046.6	Cr I	4274.8
Cd I	3610.5	Sn	3801.0	K I	4047.2	Th	4282.0
W	3613.8	Ce II	3801.5	Pb I	4057.8	Ca I	4283.1
Sc II	3613.8	Ra II	3814.4	Cb I	4059.0	Ca I	4289.4
Ni I	3619.4	Fe I	3820.4	Pr I	4062.8	Cr I	4289.7
Sc II	3630.8	Fe I	3827.8	Fe I	4063.6	W I	4294.6
Pd I	3634.7	Mg I	3829.4	W I	4074.4	W I	4302.1
Ti I	3635.5	Mg I	3832.3	La II	4077.4	Ca I	4302.5
Pb I	3639.6	Mg I	3838.3	Sr II	4077.7	Nd	4302.1
Ti I	3642.7	Co I	3842.1	Dy I	4078.0	Ti I	4305.9
Sc II	3642.8	Tb I	3848.8	U	4080.3	Fe I	4307.9
Gd I	3646.2	Rh I	3856.5	Hf I	4093.2	Sc II	4314.1
Fe I	3647.9	U	3859.6	V I	4099.8	Ca I	4318.7
Hg I	3650.2	Fe I	3859.9	Cb I	4101.0	Ce	4320.7
Sc II	3651.8	Mo I	3864.1	In I	4101.8	Sc II	4320.8
Ti I	3653.3	W I	3868.0	V I	4105.2	Sc II	4325.0
Hg I	3654.8	Co I	3873.1	Co I	4110.5	Fe I	4325.8
Rh I	3658.0	Co I	3873.9	V I	4111.8	La	4333.8
Ru I	3661.4	Tb I	3874.2	V I	4116.7	La	4334.0

TABLE II. *Continued*

U	4341.7	Be I	4572.7	Li	4971.9	Mg I	5528.5
Hg I	4358.3	Cs I	4593.2	Na I	4979.0	Mo I	5533.0
Sc II	4374.5	Ce	4593.2	Ti I	4981.7	Ba I	5535.5
Rh I	4374.8	V I	4594.1	Ti I	4991.1	Pd	5542.8
Y II	4375.0	Li I	4603.2	Ti I	4999.5	Pd	5547.0
V I	4379.2	Sr I	4607.3	Ti I	5007.2	Bi	5552.2
Mo	4381.7	Ce	4628.2	Ti I	5014.3	Mo I	5570.5
Th	4381.9	Y I	4643.7	Ti I	5016.2	Ca I	5590.1
Ce	4382.2	Ag I	4668.5	Th	5017.2	Pb	5608.8
Fe I	4383.5	Y I	4643.7	U	5027.4	Sc	5671.8
V I	4384.7	Ag I	4668.5	Sc	5031.0	Na I	5682.8
V I	4390.0	Y I	4674.8	Th	5049.8	Sc	5686.9
Sa I	4390.9	Cd I	4678.2	W	5053.3	Na I	5688.3
Th	4391.1	Zn I	4680.1	Ce	5079.7	Cu I	5700.3
V I	4395.2	Ra II	4682.2	Ni	5080.5	Hg I	5769.6
Sc II	4400.4	Zr I	4687.8	Ni	5081.1	Ba I	5777.7
V I	4400.6	S I	4694.2	Sc I	5081.6	Cu I	5782.1
Fe II	4404.8	S I	4695.5	Sc I	5083.7	K I	5782.6
V I	4406.7	S I	4696.3	Cd I	5085.8	Hg I	5790.7
V I	4408.2	Mg I	4703.1	Cu	5105.6	K	5801.9
V I	4408.5	Mn I	4709.7	Cu I	5153.2	Ta	5811.1
Mo	4411.7	Zr I	4710.1	Pd	5163.8	K	5812.4
Os I	4420.5	Ni I	4714.4	Mg I	5167.3	Au	5837.4
Sa I	4424.4	Zn I	4722.2	Ru	5171.0	Pt	5840.1
Ca I	4425.4	Bi I	4722.5	Mg I	5172.7	Mo I	5858.3
La	4429.9	Mn I	4727.5	Mg I	5183.6	Mo I	5868.3
Sa I	4434.4	Se I	4730.9	Cr I	5204.5	Na I	5890.0
Mo	4435.0	Se I	4739.1	Cr I	5206.0	Na I	5895.9
Ca I	4435.0	Zr I	4739.5	Cr I	5208.4	U	5915.4
Ca I	4435.7	Se I	4742.3	Ag I	5209.0	La I	5930.6
Nd	4446.4	Mn I	4754.1	Cu I	5218.2	Pb	6002.0
Nd	4451.6	Mn I	4762.4	W	5224.7	Mn I	6013.5
Ca I	4454.8	Zr I	4772.3	Fe	5227.2	Mn I	6016.6
Ca I	4455.9	Mn I	4783.4	Pt	5227.6	Mn I	6021.8
Ca I	4456.6	Pd	4788.2	Fe I	5232.9	Mo I	6030.7
V I	4460.3	Au	4792.6	Fe I	5269.5	Li I	6103.6
Nd	4463.0	Co I	4792.9	Pd	5295.6	Ca I	6122.2
U	4472.3	Os	4794.0	Pt	5301.0	Ba II	6141.8
Ba I	4489.0	Cd I	4799.9	Fe I	5328.0	Ca I	6162.2
In I	4511.3	Zn I	4810.5	Tl I	5350.5	Al II	6231.8
Re I	4513.3	Co I	4813.5	Pt	5360.0	Al II	6243.4
Lu I	4518.5	Zr I	4815.6	Fe I	5371.5	La I	6249.9
Ce	4523.1	Pd	4817.5	Pt	5390.8	Sc I	6305.7
Sn I	4524.7	Mn I	4823.5	Cr I	5409.8	Zn I	6362.4
Ce	4528.4	Ra I	4825.9	Ba I	5424.6	Ta	6430.8
Ce	4528.5	Sr I	4832.1	La I	5455.1	Cd I	6438.5
Rh	4528.7	V I	4851.5	Hg I	5460.7	Ca I	6439.1
Ti I	4533.3	Th	4863.2	Ag I	5465.4	U	6449.2
Ti I	4534.8	V I	4864.8	Ag I	5471.5	Ca I	6462.6
Ti I	4535.6	Co I	4867.9	Pt	5475.8	Ta	6485.4
Ti I	4535.9	Ru	4869.2	Ni I	5476.9	Ca I	6493.8
Ti I	4536.1	Sr I	4872.5	Pt	5478.5	Ba II	6496.9
Ce	4539.7	Pd	4876.4	W	5492.3	Ta	6516.1
Ba II	4554.0	V I	4875.5	U	5492.9	Li I	6707.9
Ru	4554.5	V I	4881.6	Mo I	5506.5	K I	6911.3
Cs I	4555.3	Re I	4889.2	Ce	5512.1	K I	6939.0
Ce	4562.4	Th	4919.8	W	5514.7	K I	7664.9
Mg I	4571.1	La	4921.8	Ba I	5519.1	K I	7699.0
Rb	4571.8	Ba II	4934.1	Sc	5526.8	Rb I	7800.3
Ce	4572.3	Sr I	4934.1	U	5527.8	Rb I	7947.6

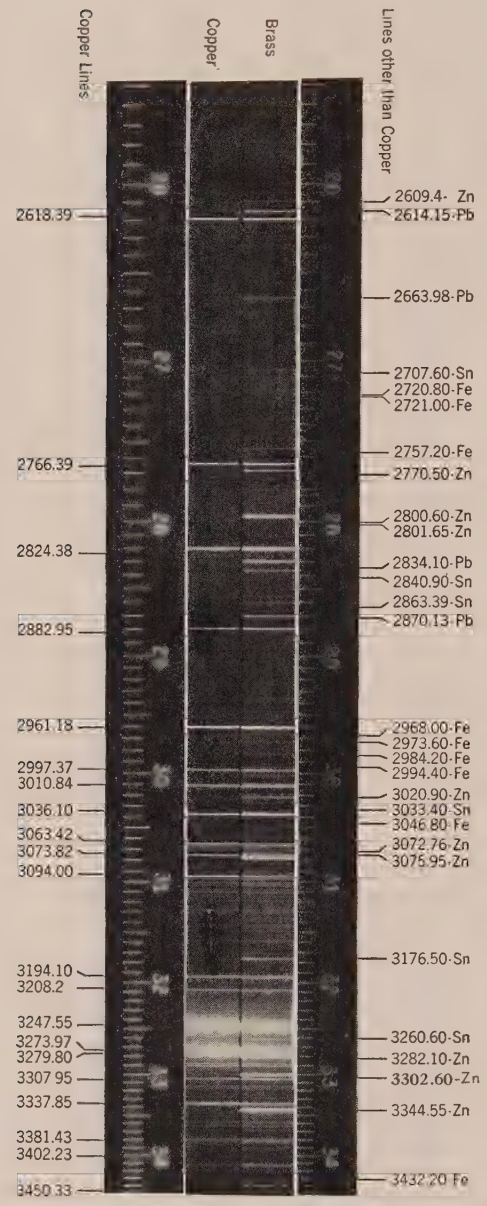

FIG. 509. Arc Spectra of Copper and Brass Samples.

able at the present time is the Eder and Valenta atlas, which includes arc, spark and flame spectra of nearly all of the available elements, taken with glass prism, quartz prism and grating spectrographs. The dispersion, however, is not satisfactory for the accurate identification of many elements, especially where the spectrum is complicated. Adam Hilger have published several photographic tables, one of which gives the persistent lines of a large number of elements. They also have published iron, copper and neon spectra in which the dispersion is high and a large number of the lines identified. To further aid in the identification of other elements, tables have been prepared in which, in addition to the iron spectrum, there is indicated the position at which a strong line of some other element would appear if it were present. Tables of this type have been published by Bardet, Crook and others. From the tables in this chapter and with the use of an accurately calibrated scale on the instrument or with an iron spectrum in contact with the unknown spectrum and a photographic identification of the iron spectrum, one can satisfy nearly all the requirements of the qualitative analysis of elements by the spectrographic method.

QUANTITATIVE ANALYSIS

de Gramont has proposed that the ultimate lines or the Raies Ultimes of the elements are to a certain degree the basic lines of the element and as such their intensity will be proportional to the amount of the element present. The first practical application of this theory to quantitative analysis was made by Meggers Kiess and Stimson in the analysis of platinum metals. In all of the suggested methods of quantitative spectrographic analysis the results are dependent on the known chemical composition of comparative standards. One might subdivide the methods into those in which the comparative standard is observed under similar conditions to that of the unknown observation, and those in which the standard substance is added to the unknown so that both photographs are made simultaneously.

Comparison with Standards.—Certain of the tentative standard and recommended methods of analysis of materials by the spectrographic method involve the comparison of line intensities between standard photographs and unknown photographs taken under similar conditions. If the conditions of exposure, development, slit, current density, and type of plate are maintained it may not be necessary to repeat the photograph of the known standard but merely to compare with a previously prepared standard negative. A certain amount of possible error can be avoided by the taking of a photograph of the standard sample adjacent to the unknown sample on the same negative. In many cases this method of comparative analysis is satisfactory. On account of the large number of variable factors which exist it is not possible to supply

standard spectra or spectrum plates for the comparison measurements, so that each worker must provide his own comparative standards.

Internal Standards.—The satisfactory results obtained in the analysis of substances by comparison photographs has led to the improvement of the

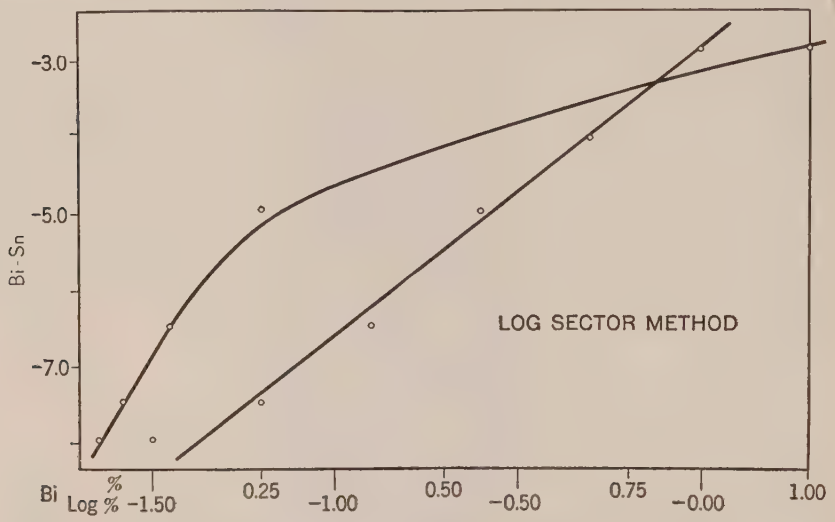

FIG. 510. Working Curve for the Analysis of Bismuth, Using Tin as the Internal Standard. Determinations made by the Log Sector Method. Bi = 2989.04 A, Sn = 3009.14 A.

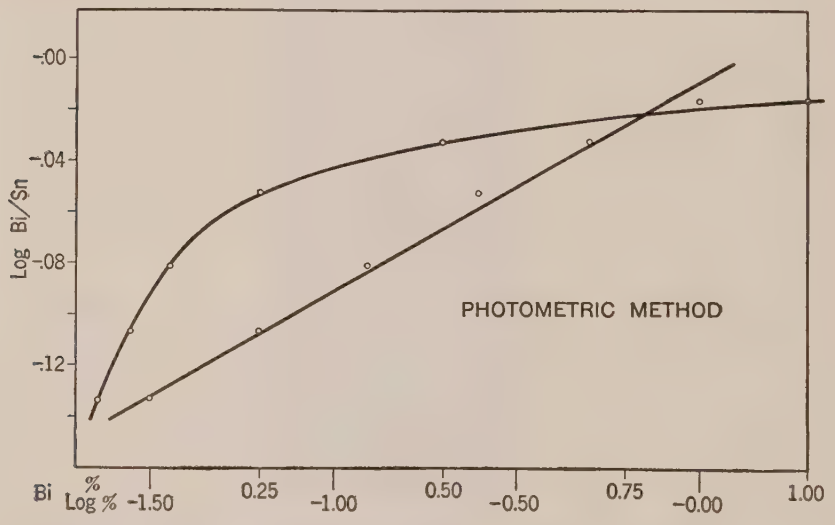

FIG. 511. Working Curve for the Analysis of Bismuth, Using Tin as the Internal Standard. Determinations made by the Photronic Cell Densitometer Method. Bi = 2989.04 A, Sn = 3009.14 A.

method by the incorporation of a standardizing substance with the material which is being analysed. This procedure eliminates many of the possible sources of error, since the two exposures are made simultaneously. The method of internal standards requires the preparation and study of a series of known mixtures and the measurement of the relative intensities of known and unknown lines. The logarithm of the ratio of line densities, plotted against the log of the concentration of the element to be analysed for, should yield a working diagram from which the concentration in an unknown sample could be determined. In Figs. 510 and 511 and Table III are given sample working curves.

TABLE III

REPORT ON WORKING CURVE DATA

Spectrographic Analysis for Bismuth

Internal Standard = Tin

Sample	% Bi	Log % Bi	% Sn	Log Sector Method			Photometer Method			Log Bi/Sn
				Length Bi 2989.04	Length Sn 3009.14	Bi-Sn	Bi 2989.04	Sn 3009.14	Bi/Sn	
1	0.000	—	—	—	—	—	—	—	—	—
2	0.000	—	1.0	—	11.5	—	—	10.05	—	—
3	0.031	−1.502	1.0	3.6	11.5	−7.9	7.5	10.18	0.736	−0.1331
4	0.063	−1.204	1.0	4.0	11.5	−7.5	7.85	10.03	0.783	−0.1062
5	0.125	−0.903	1.0	5.0	11.4	−6.4	8.40	10.10	0.832	−0.0797
6	0.250	−0.602	1.0	5.8	10.7	−4.9	8.88	10.0	0.888	−0.0516
7	0.500	−0.301	1.0	7.3	11.3	−4.0	9.3	10.0	0.930	−0.0315
8	1.000	0.000	1.0	8.5	11.3	−2.8	9.65	10.0	0.965	−0.0155

The choice of line pairs for comparison will of course determine the concentration range over which the data will best apply. Over the major portion of the working curve an accuracy to within about 5% of the amount of unknown element can be determined. For high concentration the method may be used, although this same percentage error will still hold and is usually much greater than that obtained by other analytical methods. For extremely small amounts, however, an error of 5 or even 10% of the amount present may be quite permissible.

Measurement of Intensities of Lines.—The determination of the blackening or line densities on the photographic plate may be photometrically measured by visual or electrical means. A number of recording and semi-automatic densitometers for the measurement of plate and line density are available for this purpose. These instruments may have certain constant errors such as the failure to obtain a linear response from the photo cell over a range of varied light intensities. A combination of densitometer and spectrograph can be effected by placing directly in front of the spectrograph slit a rotating sector, cut either smoothly or in steps and usually cut in a logarithm spiral or in logarithmic steps, or by the use of a step slit such as the Hansen or Duffendack type. This procedure produces a spectrogram in which the line tapers in its degree of blackening until it fades completely out, or is reduced by steps to

complete extinction. In the step system a photometer may be applied to the lines at different densities. The continuous line (Fig. 512) produced by the logarithmic spiral sector may be measured as to length with a micrometer eyepiece. The difficulty of deciding on the point of absolute extinction or

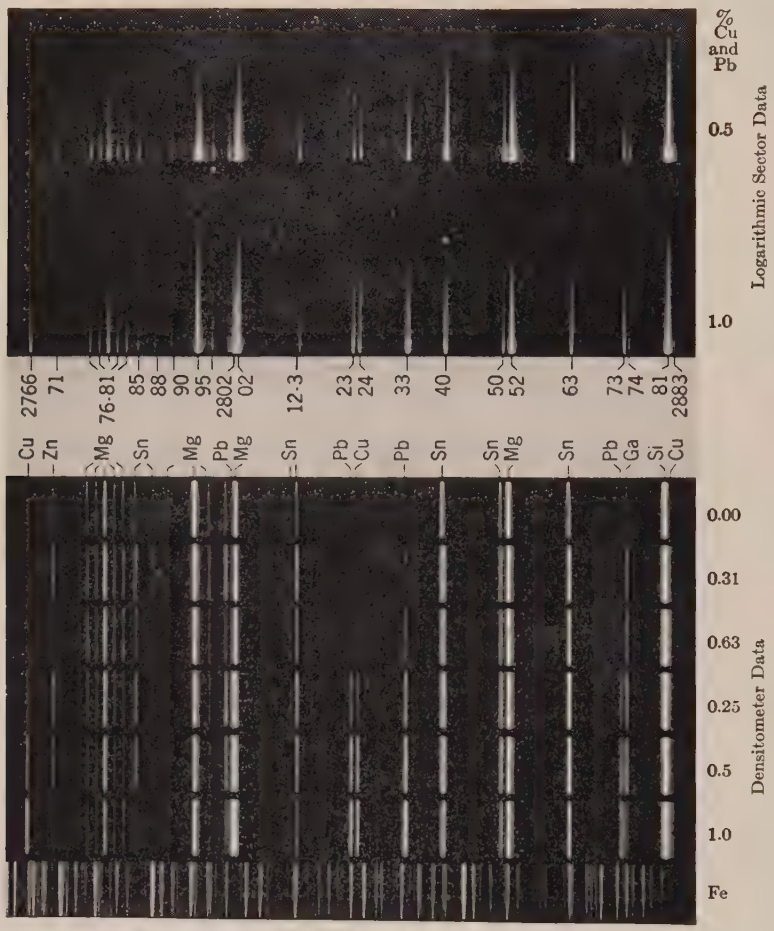

FIG. 512. Typical Spectra by Log Sector and Ordinary Spectrum Photographs Used in the Preparation of Working Curves.

termination of the line may be eliminated in part by the use of a reversed line in the eyepiece and matching the two lines to a uniform density.

In methods where comparison is to be made between spectrograms, especially where the spectrograms are on different plates, it is somewhat important to determine the plate characteristics and many workers feel that this procedure should be carried out when the data are all on the same plate. The variation

of the plate characteristics (i.e. the $d/\log I$ curve) with different spectral regions, nature of exposure, development time and temperature, etc., may require that for accurate work the plate characteristics should be determined through the use of a standard lamp for illumination of the spectrograph and that correction be made so as to indicate the absolute intensities of the lines. In routine analysis where the same plate treatment is used, the same type of plates and photometric methods, it is possible to prepare working curves which will give accurate quantitative results.

Control of Conditions.—An important working condition in quantitative spectrographic analysis which must be carefully controlled involves the light source. From a study of the cause and nature of spectrum lines it will be noted that there are successive stages of ionization of the element, which are dependent on the applied voltage and temperature. The spectrum produced under low ionization conditions may be quite different in the lines present and their intensities as compared with the spectrum from the highly ionized element. This change in relative intensities of the emission lines with a change in exciting conditions requires a careful duplication of conditions when making a series of observations, and requires a rather exact definition of the exciting conditions if one is to apply the working curve or analytical data prepared and published by others. Gerlach has attempted to define the working conditions by which repeated observations could be made, through the selection of lines of the known element from different states of ionization, which at the given conditions of observation are equal in intensity. When they are equal the excitation can be said to be at the standard or specified condition. Gerlach has then varied the amount of "unknown" element with respect to the internal standard (the internal standard may be the element present in largest amount or an added standard of known amount) and selected for each concentration pairs of lines of the standard known and unknown which are of equal intensity. These pairs are known as homologous pairs. In view of their equal intensity it can be seen that these results will not be appreciably influenced by plate characteristics and other errors which have been mentioned. If the internal standard is to be some element other than the substance present in largest amount (the pure substance containing the impurity for which the analysis is being made) it will be necessary to control the amount of internal standard which is added. This is accomplished by choosing a pair of lines, one from the pure or base substance and the other from the internal standard, which are equal in intensity under the excitation and concentration conditions which are used for the observation. This method may be better understood from Table IV which is a portion of an analyses table published by Scheibe.

TABLE IV

Quantitative analysis for Titanium in an Aluminum sample. Control of excitation conditions Al II 2616.18 = Al I 2575.11 Å. Internal standard control or coupling, pair Al I 2652.48 = Cu 2618.38 Å.

Wavelength Titanium	Wavelength Copper	Percent of Ti in Sample when Lines Are of Equal Density
Ti II 3361.22	3307.95	0.26
Ti II 3361.22	3337.85	0.204
Ti II 3335.19	3349.26	0.188
Ti II 3361.22	4022.70	0.166
Ti II 3361.22	3365.36	0.109

It would seem that while this method may have eliminated a number of the possible errors of other methods it involves the setting up of definite conditions of excitation, internal standard concentration and line intensity measurement, which in the end are required of nearly all methods which give reproducible results. In the method described by Gerlach the spectrum of the so-called internal standard may be taken separately, either on top of or adjacent to the sample to be analysed and need not be that of a mixture of the sample and internal standard, just so long as the homologous and coupling or control pairs are equivalent in density.

In order to control more carefully and standardize the spectrographic data in an analysis, Duffendack and his coworkers have developed the use of plate calibration through the use of a step slit so as to remove possible errors which might result in the failure of the negative to yield a linear d-log I curve and of the same slope for all wavelength values.

It would seem that while the method of quantitative spectrographic analysis has been rather carefully studied and applied to a large number of problems with considerable success, it is not possible to give such specific data as is available for qualitative spectrographic analysis in the wavelength tables. Because of the nature of the method it is necessary in nearly all cases to prepare standard negatives, mixtures or working curves which apply to the particular spectrograph, photographic plate, photometer or other influencing factors. The value of published work in the field of quantitative spectrographic methods lies largely in the development of technique and the experimental determination of satisfactory groups or pairs of lines for specific analytical purposes.

Plates.—For the usual type of qualitative or quantitative spectrographic analysis a medium speed photographic plate such as the Eastman 33 or 40 is quite satisfactory. Development can be by elon-hydroquinone (metol-hydroquinone) or other standardized developer. For spectral regions beyond 5000 A panchromatic or special red sensitive negatives are available to about 14,000 A.

ABSORPTION SPECTRA

When an object or solution absorbs a portion of the homogenous spectral radiation which passes through it we describe the material as being colored. The absorption of homogenous spectral radiation by molecules is usually quite selective and limited to definite spectral regions, or bands. These absorption bands are usually diffuse, with partial absorption over a considerable region and a gradual increase in absorption to a maximum of absorption near the center of the absorption band. The intensity and position of the absorption maximum, as well as the rate of increase in absorption on each side of the maximum are definite properties of the compound being examined and may serve to identify or characterize the substance. Within the visible spectral region one might indicate the production of color by absorption bands as follows:

TABLE V

RELATION BETWEEN ABSORPTION BAND POSITION AND OBSERVED COLOR

Position of Absorption Band	Color Absorbed	Color Transmitted
450 mμ	Blue	Yellow
500	Blue-Green	Orange
550	Blue-Green-Yellow	Red
600	Green-Yellow	Red and Blue
650	Yellow-Orange	Blue
700	Red	Blue-Green
400 and 750	Blue and Red	Green

Since absorption bands are usually not well defined like emission lines it is the practice to record wave length values in millimicrons ($m\mu = \text{meters} \times 10^{-9}$). For work in the ultraviolet region the data is often recorded in frequency or wavenumber, since absorption bands represent in many cases harmonic vibrations which give regularly spaced bands on a frequency scale.

The intensity of absorption is an important value for the quantitative estimation of the absorbing material. Where one is interested in a description of the transmitted color one usually records the per cent of light transmitted at various wavelength values. If one is interested in the amount or character of the absorbing substance one usually records the extinction coefficient. The extinction coefficient may be defined as the Log of the incident intensity divided by the transmitted intensity ($\log I_0/I$). By recording in extinction coefficient values, the height of the absorption band is directly proportional to the concentration or cell thickness (assuming that Beer's law holds for the material). From the extinction coefficient of the maximum of the absorption band of a substance one may obtain a much more accurate value for the concentration than through a colorimetric measure of the transmitted light. In addition, the position and shape of the curve may enable one to identify the molecule producing the absorption. The production of absorption is dependent on the presence in the molecule of an absorbing or chromophoric group. Not all substances absorb radiation within the visible or photographic ultraviolet region, and hence it is possible to detect and identify traces of absorbing materials in otherwise transparent materials. For example, it is possible to detect and quantitatively estimate the amount of benzene present in ethyl alcohol, with an accuracy of about 10% of the amount present, when the concentration may be as low as 0.001%. The spectrophotometer has been used in the quantitative estimation of such colored inorganic substances as cobalt, iodine, copper, and the rare earths (Fig. 513). For the purpose of estimation of impurities and their detection one may use the method of subtractive absorption in which one subtracts the absorption band of the known pure substance from the observed band, the difference representing the impurity absorption (Fig. 514). Commercial dyestuffs are standardized and their concentration determined by absorption spectra methods which give rapid and accurate quantitative results. Much of the synthetical work in the fields of vitamins, hormones and natural pigments is based on the absorption spectra data obtained by the study of these and related compounds.

The data in the field of absorption spectra measurements is so varied that it is not possible to give methods of procedure and interpretation of data. For a more detailed discussion of these fields one should consult the references in the bibliography which follows.

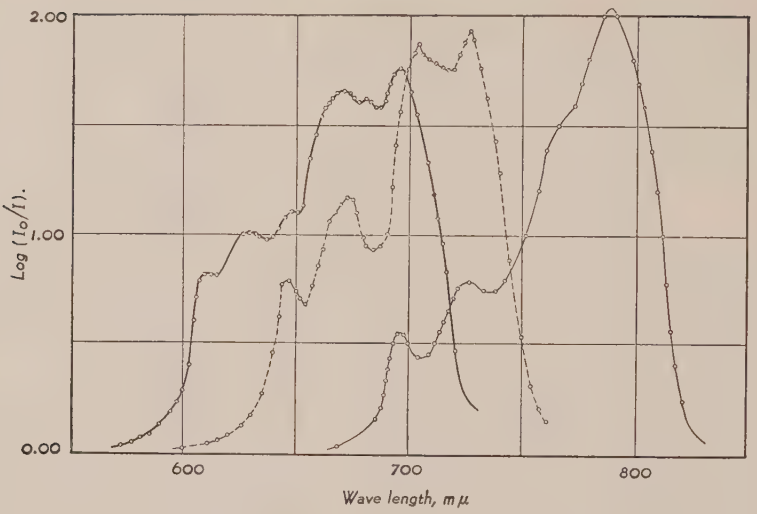

FIG. 513. The Absorption Spectra of Cobaltous Halides in their Corresponding Halogen Acids ——— $CoCl_2$ in HCl; – – – – – $CoBr_2$ in HBr; ——— CoI_2 in HI. (Brode, J. Am. Chem. Soc., **53**, 2457 (1931).)

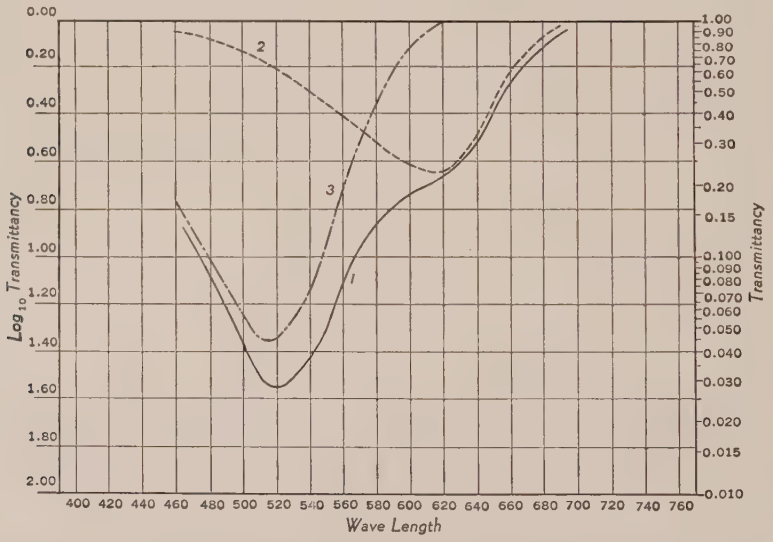

FIG. 514. Identification of Impurities in Commercial Dyestuffs. (1) Mother liquor absorption from a 16% dyeing of a commercial sample of Agalma Black 10B whose shade was rated as RRR by dyeing tests. (2) Absorpton spectrum of the pure dye. (3) Difference curve or absorption spectrum of impurity. (Note. Data are recorded in -log Transmittancy which is the same as extinction coefficient but plotted as a negative value.) (Brode, Ind. Eng. Chem., **18**, 708 (1926).)

Special Note—Patent Situation.—Users of spectrographic methods of analysis, including both for non-profit research as well as commercial applications, should be cognizant of the existence of U. S. Patent No. 1,979,964 (application made March 14, 1932 and granted Nov. 6, 1934) by Duffendack and Wolfe. The claims include the following:

"1. The method of quantitative spectroscopic analysis which comprises the following steps: establishing an arc current between electrodes comprising the unknown material of value such that the intensity of spectral lines does not vary materially with unavoidable fluctuations in arc current, recording the spectrum of the arc, measuring the ratio of intensities of a pair of lines in the spectrum by comparison of the strengths of the corresponding recorded lines, repeating the process with a series of electrodes containing the same kind of material but of known analysis, making use of the same spectral lines, evaluating the ratio of intensities obtained from the unknown material in terms of percentage of an element producing one of the lines by comparing the ratio of intensity of the unknown with the ratio of intensity of said known specimens."

In following claims the use of a spark and luminous discharge are covered as well as the recording of the spectrum on a photographic plate. In view of the large amount of previously published work in the field of spectrographic quantitative analysis, much of which is referred to in the patent, it seems unfortunate that a patent claim should be granted which rather effectively covers the fundamental principles involved in this analytical field. It seems unfortunate that basic claims in patents should be granted for analytical methods, especially if the methods have been widely used and published in the literature.

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SOLUBILITY TABLE

SOLUBILITY TABLE*—GRAMS OF (ANHYDROUS)

Cation → / Anion ↓	NH_4^+	Hg^{++}	Hg^+	K^+	Na^+	Li^+	Sn^{++}	Sn^{++++}	Bi^{+++}	Cd^{++}	Pb^{++}	Zn^{++}	Sb^{+++}	Mg^{++}	Al^{+++}	Ca^{++}
F^-	d	d	d	57.0	25° 4.05	25° 0.15	A	W	W	25° .622	25° 0.66	25° 1.51	1.6	25° .013	25° .559	25° .004
Cl^-	35.2	7.32	.0₃1	33.4	35.9	77.0	275.	W	d	92.0	.914	362.	.602	54.1	41.0	72.5
Br^-	15° 66.0	0.4	.0₃4	64.1	89.0	174.	W	W	d	75.5	0.80	441.	d	96.1	46.5	148.
I^-	167.	.003	.0₇2	142.	176.	163.	10.0	W	A	15° 89.0	.066	432.	d	148.	W	166.
ClO_3^-	W	W	.001	6.7	97.0	213.	W	W	W	76.3	151.	198.	d	130.	W	177.
BrO_3^-	W	16.0	d	6.5	34.0	153.	A	A	—	A	1.34	53.0	d	80.0	—	85.0
IO_3^-	15° 26.0	.001	.001	7.5	8.5	80.3	A	A	—	A	.001	0.9	d	12.0	—	0.26
NO_3^-	0° 118.	W	d	29.6	86.0	70.3	W	d	d	15° 127.0	50.7	116.	d	73.2	W	121.
$C_2H_3O_2^-$	148.	10° 25.0	13° 0.75	245.	47.0	**	A	—	W	W	50.0	27° 40.0	d	W	W	35.0
OH^-	W	—	**	110.	107.	128.	.0₃1	A	.0₃1	.0₃2	.015	.0₃6	d	.0₃8	A	.167
O^{--}	d	15° .055	A	d	d	0° 5.0	A	A	A	A	.068	.0₃1	.0₄2	.0₃6	A	0.13
S^{--}	27° 100.	.0₃2	d	W	15.3	.009	.0₃2	.0₄2	.0₄18	.0₃13	.0₄8	.0₃7	.0₄18	d	d	d
CO_3^{--}	15° 100.	.001	.001	111.	19.5	1.3	—	—	A	A	.001	.001	d	.095	Alk	.001
SO_4^{--}	15° 74.2	d	.06	10.7	16.8	34.4	18.4	6.0	A	15° 59.0	.004	53.0	d	34.6	26.7	.202
$C_2O_4^{--}$	4.2	A	A	2° 37.2	3.5	25° 6.2	A	W	A	.003	.0₃15	.0₃6	A	0.03	A	.0₃5
CrO_4^{--}	30° 40.5	d	A	62.5	77.5	110.	A	—	A	A	.042	**	A	72.3	A	23.4
PO_4^{---}	50° 22.0	A	A	—	19.6	.04	A	A	A	A	.0₄14	**	A	**	A	**
AsO_4^{---}	W	A	A	15° 18.8	10.4	W	—	A	A	—	A	A	A	A	A	A
$Fe(CN)_6^{----}$	W	A	—	28.0	15° 22.0	W	I	I	—	—	A	A	d	W	—	**

* Metals arranged in order of increasing melting point.

W = soluble in water; A = soluble in acids; AR = soluble in aqua regia; d = decompose; Alk = soluble in alkalies; I = insoluble in water or acids; ** = solubility less than 0.01 gm. per 100 ml. of water; — = solubility very small and not definitely known.

Decimals have been indicated .0₄2 = 0.00002; numbers indicate gm. of the anhydrous salt dissolved in 100 ml. of water, at 18° C., unless otherwise specified.

SOLUBILITY TABLE

SALT PER 100 ML. OF WATER AT 18° C.

Sr^{++}	Ba^{++}	Ag^{+}	Au^{+++}	Cu^{++}	Mn^{++}	Ni^{++}	Co^{++}	Fe^{++}	Fe^{+++}	Cr^{+++}	V^{++}	Pt^{++++}	Ti^{++++}	Mo^{++++}	W^{++++}	←Cation Anion ↓
25° .039	25° .121	183.	d	25° .073	25° .186	25° 4.03	25° 1.41	A	.091	W	d	AR	d	d	d	F^-
52.8	35.2	$.0_31$		75.6	10° 107.	64.0	5.0	41.5	74.4	W	W	AR	d	d	d	Cl^-
98.0	103.	$.0_58$	d	W	127.	130.	4.61	53.5	W	W	—	0.41	d	W	—	Br^-
176.	195.	$.0_63$	d	W	d	59.1	31.0	W	W	W	—	I	W	W	A	I^-
175.	35.5	10.0	d	164.	W	56.7	0° 135.	W	W	W	—	—	—	W	—	ClO_3^-
33.0	0.6	.144	d	W	W	27.6	—	—	—	—	—	—	—	W	—	BrO_3^-
.026	0.02	.004	d	.121	W	1.01	—	—	—	—	—	—	—	—	—	IO_3^-
67.6	8.8	121.0	d	120.	100.	50.	100.	46.0	W	W	—	d	—	A	—	NO_3^-
.004	60.7	1.8	—	7.2	A	16.6	A	A	.023	A	—	—	W	—	—	$C_2H_3O_2^-$
0.78	3.58	.002	A	**	$.0_39$	Alk	A	$.0_36$	A	Alk	—	Alk	A	—	—	OH^-
0° 35.0	1.5	.002	A	A	$.0_36$	A	A	A	A	A	A	A	I	.106	Alk	O^{--}
d	d	$.0_43$	AR	$.0_43$	$.0_36$	$.0_33$	$.0_34$	$.0_38$	$.0_51$	d	—	A	A	Alk	W	S^{--}
.001	.002	.003	—	.001	.006	.009	A	**	d	**	—	—	—	—	—	CO_3^{--}
.011	$.0_32$	.775	d	19.9	0° 53.7	36.5	15° 32.0	26.4	W	120.	0.80	d	—	W	—	SO_4^{--}
.004	.008	.003	A	**	.07	A	A	.022	A	A	—	W	—	—	—	$C_2O_4^{--}$
0.12	$.0_32$	.002	—	**	W	A	A	.022	W	A	—	—	—	—	—	CrO_4^{--}
**	**	.001	—	**	0.02	A	A	A	A	A	—	—	—	—	—	PO_4^{--}
A	.055	$.0_48$	—	A	A	A	A	A	A	A	—	A	—	—	—	AsO_4^{---}
W	A	$.0_46$	—	I	A	I	I	A	A	Alk	—	—	—	—	—	$Fe(CN)_6^{----}$

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